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MECHANISM OF THE ACTION OF ALKALINE IODINE SOLUTION ON ACETALDEHYDE

By

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Woo and Chuld[10] have suggested that the iodoform reaction of acetaldehyde is probably accompanied by oxidation of the aldehyde molecule to acetic acid. The present worker[4] by an analytical study of the action of alkaline iodine on acetaldehyde has shown that two simultaneous reactions occur:

$$CH_3CHO + 3 I_2 + 4 NaOH = CHI_3 + HCOONa + 3 NaI + 3 H_2O \quad (1)$$

$$CH_3CHO + I_2 + 3 NaOH = CH_3COONa + 2 NaI + 2 H_2O \quad (2)$$
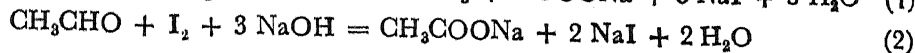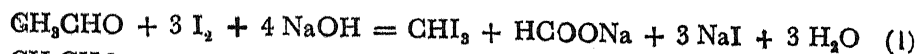
In presence of plenty of free alkali the first reaction was predominant while in presence of free iodine and low alkali concentration the second one occured to a larger extent. So far no attempt has been made to explain this peculiar phenomenon nor any mechanism proposed for the formation of iodoform from acetaldehyde. Bell and Longuit-Higgins[2] investigated the formation of iodoform from acetone. They studied the base catalysed halogenation of acetone and observed that the rate determining step was the transfer of a proton from acetone to the basic catalyst present because the reaction was zero-order with respect to the halogenating agent (iodine) and first order with respect to both acetone and hydroxyl ions. Bartlett[1] who also found that the reaction rate depended on acetone concentration and on the free alkali present in the solution, assumed that the reaction involved the enolisation of acetone ($CH_2=C.OH.CH_3$). As this enolisation was catalysed by free alkali, the reaction depended more on alkali concentration. Although the acetaldehyde reaction also depends on the alkali concentration, a similiar enolisation is improbable from its electronic structure considerations. Ingles and Israel[3] undertook the kinetic

study of the hypoiodite oxidation of several aldoses (glucose mannose, galactose etc.) and concluded that the effective oxidising agent was the unionised HIO present in the solution. In the present study the amount of iodine consumed and the iodoform produced were estimated under varying pH and the results correlated with the concentrations of the OI⁻ ions and unionised HIO molecules in the reaction mixture.

EXPERIMENTAL

The boiling point of acetaldehyde being very low it is not possible to prepare its standard solutions by weighing. Stock solution of 0·05 M acetaldehyde was prepared by dissolving a pure sample of the aldehyde in conductivity water and this solution was standardised by (a) Schults[9] hydroxylamine sulphate method and (b) hypoiodite oxidation method.[8] The two methods gave results which agreed to 1% accuracy. The second procedure was quick and accurate and gave good results even with very dilute solutions for which Schults method was found to be unsuitable.

(A) Dependance of iodine consumed on pH of the solution :

Three sets of experiments were carried out at 3 different dilutions of acetaldehyde and iodine, and the amount of iodine cousumed under varying pH, determined. In the first set 10 c. c. of 0 002 M acetaldehyde and 10 c.c. of 0·0125N iodine solutions were mixed and diluted with 50 c.c. of water. The reaction was started by adding 4 N sodium hydroxide solution (varying quantities). The pH of the reaction mixture was immediately determined by Beckman pH meter Model H2. The solutions were stirred up before taking the pH reading. As the concentrations of acetaldehyde and iodine were very low as compared with that of the alkali, there was only a very slight change in pH (∓ 0·1) during the course of the reaction in these experiments. After 15 minutes (at 25° C) when the reaction was complete the reaction mixture was acidified with excess of 4N sulphuric acid and the iodine liberated titrated with 0·0125 N sodium thiosulphate solution. A blank was carried out under identical conditions except for the addition of acetaldehyde.
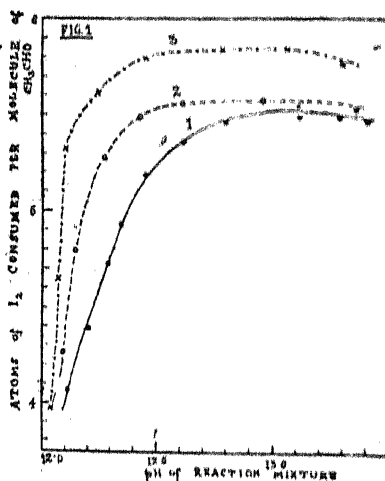
The other two sets of experiments were similarly carried out but the water used for the purpose of dilution was 100 and 200 c.c. respectively for the second and third sets. Fig 1 shows the fluctuations in the amount of iodine consumed which

occur with the variation in the pH of the reaction mixture. The large increase in the amount of iodine consumed with increase of pH is noteworthy. This predicts more and more of iodoform formation with increase in alkalinity.

(B) Dependance of iodoform formed on pH :

In these experiments the iodoform produced was estimated by photo-oxidation[5] as the amount produced was very small and could not be estimated by the usual methods. The reaction was carried out in the manner already described under varying pH which was experimentally determined. At the end, after acidifying the reaction mixture the excess of iodine liberated was titrated precisely with sodium thiosulphate solution and then the iodoform present was repeatedly extracted with about 50 c.c. of ether. This solution of iodoform was taken in a 250 c.c. pyrex flask and treated with 10 c.c. benzene and 100. c.c. of 0·01 N sodium thiosulphate solution. The flask was exposed to sunlight at about 25°C for half an hour with shaking at intervals. At the end the ether benzene layer remained colourless indicating that all the iodoform had decomposed. The excess of sodium thiosulphate in the flask was then titrated with iodine solution and thus the iodine liberated by the quantitative oxidation of iodoform was determined (one molecule of iodoform gave three atoms of iodine). The method has a precision of 1% or better. In Fig. 2 the percentage
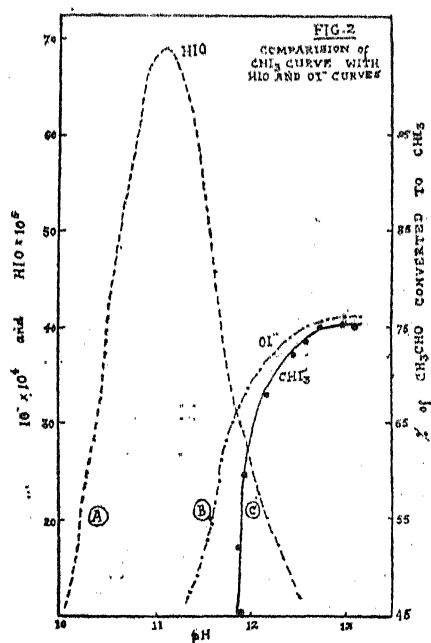
of acetaldehyde converted to iodoform has been plotted against pH of the reaction mixture.

DISCUSSION

The iodoform reaction (equation 1) consumes 6 atoms of iodine per molecule of acetaldehyde while the oxidation reaction (equation 2) consumes 2 atoms. In Fig. 1 increase in alkalinity leads to an increase in the consumption of iodine and the atoms

of iodine consumed per molecule of acetaldehyde rises to 5·8, approaching the theoretical value of 6. In Fig. 2 the experimental curve (C) has been compared with the theoretical curves (A) obtained by plotting the concentration of unionised HIO molecules against pH and curve (B) obtained by plotting concentration of OI⁻ions against pH. The curves A and B have been adopted from the paper, published by Ingles and Israel (*loc cit*). It will be evident from the slope of the curves that the iodoform curve (C) resembles very much the OI⁻curve (B) and differs very markedly from the HIO curve. This shows that the increase in the OI⁻ions between pH: 12-12·5 is responsible for corresponding increase in the formation of iodoform.

The preliminary value of the ionisation constant of HIO has been given by Firth[7] as:

$$Ka = \frac{H^+ \times OI^-}{HIO} = 10^{-11}$$

Therefore the hydrolysis constant (Kh) at 25° C of NaOI will be 10⁻³. On calculating it can be shown that at pH 7 there will be 10000 molecules of unionised HIO for every OI⁻ion while at pH 13 for every one molecule of unionised HIO there will be 100 ions of OI⁻. Hence in a mixture of iodine and alkali the pH of the solution has a very marked effect on the concentration of HIO and OI⁻ which appear to be responsible for formation of acetic acid and iodoform respectively in these reactions. A mixture of iodine (40 c.c. of 0·05 N soln.) and NaOH (1 c. c. of 1N soln.) containing excess of the former reagent has a pH of about 10·5 and contains OI⁻ ions in very low concentrations. This mixture was found to act only as an oxidant and was capable of oxidising 99·7% of acetaldehyde to acetic acid. Hence a method[a] was devised for estimating acetaldehyde by iodometry by quantitatively oxidising it to acetic acid. In presence of large excess of alkali (pH about 12·5) iodine was found to convert 97% of acetaldehyde, present in very dilute solutions, to iodoform. This constitutes a second method[6] of estimating acetaldehyde iodometrically.

In conclusion it is stated that the oxidising action of a mixture of iodine and NaOH is due to unionized HIO molecules present in the solution and the iodinating action due to OI⁻ions.

SUMMARY

Alkaline iodine solution when treated with an aqueous solution of acetaldehyde produces two simultaneous reactions. One is the oxidation reaction leading to the formation of acetic acid and the other is the iodination reaction affording iodoform. A study of these two reactions (involving the estimation of iodoform by photo-oxidation) was carried out under various pH and graph drawn by plotting the iodoform produced against pH of the solution. This graph when compared with the theoretical curves obtained by plotting OI⁻ and HIO concentrations against pH of a solution of NaOI, leads one to the conclusion that the oxidation reaction is brought about by the unionised HIO molecules and the iodination reaction by the OI⁻ ions.

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CHEMICAL EXAMINATION OF THE LEAVES OF *COCCULUS LAEBA*, D. C.

PART III : STUDIES ON UNSAPONIFIABLE MATTER

By

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β and γ-sitosterols have been isolated from the leaves of *Cocculus Laeba* and have been characterised by the preparation of their acetate, benzoate and digitonide derivatives and by comparison of their analyses, m p.'s and rotations with those for known sitosterols.

Under the reasearch programme on systematic examination of Indian medicinal plants, it was thought desirable to investigate *Cocculus Laeba*, D. C. (N. O. *Menispermaceae*), a scandent shrub found in the dry parts of western India and commonly known as Ullar-billar. The plant is known for its medicinal properties[1,2] and the leaves are used for its bitter, tonic and antiperiodic properties. A preliminary chemical examination of the leaves showed the presence of alkaloids, essential oil, sterols, mucilage, colouring matter and mixture of fatty acids.[3] The present communication is concerned with the investigation of the unsaponifiable matter of the leaves and isolation of β and γ-sitosterols.

The sterols of the leaves of this plant have been isolated by the usual procedure[4] and purified by repeated crystallisation from methyl alcohol. The crude sterol fraction was further purified by extraction with methyl alcohol and by column chromatography over Brockmann alumina using petroleum ether, ether-alcohol (equal vols.) and benzene-chloroform (3:2 v/v) as the successive eluents. Two fractions of the sterol were obtained from the latter two solvents and were repeatedly recrystallised from the respective solvents. The two fractions gave the usual tests for the sterols and were identified as β and γ-sitosterols. Melting points were taken on a Kofler block and rotations were measured in chloroform solutions (conc. 1%).

EXPERIMENTAL

Isolation; purification and fractionation of sterol :

The sterol fraction was isolated by following the procedure adopted for the leaves of *Tinospora Crispa*[4] when the crude sterol fraction, yield 0·05% (on dry wt. basis of the leaves) was obtained. The crude sterol fraction was purified by repeated extraction with methyl alcohol and by column chromatography of the product over Brockmann alumina column using petroleum ether, ether-alcohol (1:1 v/v) and benzene-chloroform (3:2 v/v) as the successive eluents when two fractions A and B of the sterol were obtained from the latter two solvents. The sterol fractions were separately repeatedly recrystallised from the respective solvent mixtures. The petroleum ether extract consisted of a waxy material melting indefinitely, 50°-66°.

Examination of sterol fraction A :

The sterol fraction, obtained from ether-alcohol mixture, constituting 65% of the crude sterol was finally recrystallised from methyl alcohol when shining flakes, m.p. 136°, $[\alpha]_D^{25}$ - 37°.0 were obtained. It showed no alteration in specific rotation on crystallisation by the technique of Anderson[5]. (Found : C, 84.00; H. 11·90% M. W. (cryoscopic in benzene) 418; Calc. for $C_{29}H_{50}O$: C, 83·98; H, 12·15%, M. W. 414).

The sterol acetate, benzoate and digitonide prepared in the usual manner were obtained in shining flakes, m.p. 126°, $[\alpha]_D^{25}$ - 42°.0 (Found : C, 81·40; H, 11·39% M. W. 460. Calc. for $C_{31}H_{52}O_2$: C, 81·57; H, 11·47%, M. W. 456); m.p. 144°.0, $[\alpha]_D^{25}$ - 14.°5 (Found: C, 83·20; H, 10·38%, Calc. for $C_{36}H_{54}O_2$: C, 83·34; H. 10·49%) and as a white flocculent powder m.p. 230° (decomp.). (Found : C, 61·88; H, 8·54%. Calc. for $C_{29}H_{50}O.C_{56}H_{91}O_{29}$; C, 62·19; H, 8·65%) respectively.

The regenerated sterol obtained on hydrolysis of the sterol derivatives was found to contain the original characteristics of the sterol fraction A. The sterol has thus been identified as β-sitosterol[6] from a comparison of the analyses, m.p.'s and rotations with those for known sitosterols.

Examination of sterol fraction B :

The second sterol fraction obtained from benzene-chloroform solvent was crystallised several times from methyl alcohol till it showed no alteration in specific rotation on crystallisation by the technique of Anderson.[5] It was obtained in colourless shining plates, m.p. 145°, $[\alpha]_D^{18}$ - 40°.O, M. W. (cryoscopic in benzene) 418. (Found: C, 83·78; H, 11·98%. Calc. for $C_{29}H_{50}O$: C, 83·98; H, 12·15%, M. W. 414)

The sterol acetate and benzoate, prepared in the usual manner were obtained in colourless shining plates, m.p. 140°, $[\alpha]_D^{18}$ - 40°.0 (Found : C, 81·45; H, 11·36% Calc. for $C_{31}H_{52}O_2$: C, 81·57 ; H, 11·47%) and m.p. 150°, $[\alpha]_D^{18}$ - 14°.5 (Found : C, 83·30; H, 10·36% Calc. for $C_{36}H_{54}O_2$: C, 83 34; H, 10·49%) respectively. The sterol digitonide was obtained as a white powder, m.p. 220° (decomp.). (Found : C, 61·82; H, 8·43%. Calc. for $C_{29}H_{50}O. C_{56}H_{92}O_{29}$: C, 62·19; H, 8·65%).

The regenerated sterol obtained on hydrolysis of the sterol derivatives had the same characteristics of the original sterol in each case. The sterol has been identified as γ-sitosterol.

The characteristics of the two sterols are in conformity with the earlier observations of the author[6] on β-sitosterol from *Pongamia Glabra* and Chakravarti, *et al*[7] on γ-sitosterol from the leaves of *Aegle Marmelos Correa* respectively.

[99]

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PREPARATION OF SOME 3-ACETOXYMERCURIARYL-2-ACETOXY-MERCURIARYLIMINOTHIAZOLID-4-ONES

By

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ABSTRACT

Fungus or mold action causes loss by destruction, deterioration, weakening etc. of a large number of items of our daily need. Therefore, it is necessary to have available various fungicides from which may be chosen one or more adapted to known or anticipated conditions. With this aim in view the present author has started the fungicidal assay of several compounds likely to possess fungicidal activity. The present paper deals with the preparation of several 3-acetoxymercuriaryl-2-acetoxymercuriaryliminothiazolid-4-ones for evaluating their fungicidal properties. The conditions for obtaining the best yields have also been described.

Usefulness of thiazolidones in medicine as local anaesthetics, inhibitors of electrically induced and metrazol induced convulsions and amoebacidal agents is well recognised. Rout and Pujari[1] and Rout[2] have assayed several 2-aryliminothiazolid-4-ones and their derivatives for fungicidal activity and found that the mercurated compounds were very effective, completely inhibiting spore germination even at a dilution of 5 to 6 p. p. m. 3-Aryl-2-aryliminothiazolid-4-ones are quite similar to the corresponding 2-aryliminothiazolid-4-ones as all these compounds contain N-C-S grouping, characteristic of many well known compounds showing toxicity to fungi.[3] Further it has been recently found that 3-aryl-2-aryliminothiazolid-4-ones and 3-arylthiazolid-2, 4-diones show marked antifungal activity.[4] Several workers have earlier observed that the introduction of acetoxymercuri group or hydroxymercuri group in the nucleus, substantially augments the fungicidal as well as bactericidal properties of the parent compounds[5][6]. It was thought therefore, to prepare acetoxymercuri derivatives of some 3-aryl-2-aryliminothiazolid-4-ones in order to evaluate their antifungal activity. On the basis of earlier work on the mercuration of thiazolid-4-ones and thiazolid-2, 4-diones[7][8], it has been assumed that the acetoxymercuri group enters the aryl nuclei attached to the imino group at C_2 and N atom of the thiazolid-4-one nucleus, at the para-position or the ortho-position of the aryl nucleus (with respect to N atom), the latter case being only favoured when the para position is blocked.

The rate of formation of these compounds varies with the different thiazolid-4-ones. In some cases good yields are obtained by carrying the reaction either in hot condition or in cold condition, but in majority of cases heating becomes necessary in order to get good yields. Not only this but it considerably reduces the time taken for the completion of the reaction. This has been illustrated by preparing diacetoxymercuri derivatives of 3-phenyl 2-phenyliminothiazolid-4-one and 3-o-methylphenyl-2-o-methylphenyliminothiazolid-4-one in cold as well as in hot conditions.

EXPERIMENTAL

Preparation of the starting materials : The 3-aryl-2-aryliminothiazolid-4-ones were prepared by reacting sym-dirayl-thiocarbamides with monochloroacetic acid in ethanolic medium in the presence of anhydrous sodium acetate as discussed earlier[9][10]. The sym-diaryl thiocarbamides required for the above purpose were obtained by the method of Rathke[11] and Rao.[12]

Preparation of 3-Acetoxymercuriphenyl-2-acetoxymercuriphenyliminothiazolid-4-one : 3-Phenyl-2-phenyliminothiazolid-4-one (0·5 g.) was dissolved in alcohol (5 c. c.) and glacial acetic acid (10 c. c.) and was then heated with a warm solution of mercuric acetate (1·19 g. in 5 c. c. water and 2 c. c. acetic acid). The mixture was stirred vigorously, the compound began to separate after 5 minutes and after 20 minutes a larger portion was separated. It was then kept overnight. The precipitate was collected and washed repeatedly with hot water and finally with dilute acetic acid and hot alcohol. The compound was obtained in the form of a light yellow powder. Yield: 1·28 g. (80% of theory). It turns yellow at 190°, shrinks at 235° and decomposes above 250°C.

Found: Hg, 52·30. $C_{19}H_{16}N_2O_5SHg_2$ requires Hg, 51·07 per cent.

This compound was also prepared by the following method:

SECOND METHOD

The reactants were taken in the same proportion as described in the above experiment, in a 100 ml. hydrolysis flask and refluxed directly on an asbestos wire-gauze. After refluxing for two minutes a dirty white material began to separate. The rate of separation of this compound increased with time. After ten minutes, refluxing was stopped and after cooling, excess of water was added, when further precipitation occured. The compound was filtered on a Buchner funnel and was treated as indicated under the First method. Yield: 1·23 g. (77% of theory). This also darkens in colour and then shrinks at 235-36° and decomposes above 250°C. Found: Hg, 51·88. $C_{19}H_{16}N_2O_5SHg_2$ requires Hg, 51·07 per cent.

After a careful study of the above two methods it becomes obvious that 3-acetoxymercuriphenyl-2-acetoxymercuriphenyliminothiazolid—4-one is formed in nearly equal yields by both the methods but by applying second method the reaction is completed within 10 minutes only.

Preparation of 3-Acetoxymercuri-o-methylphenyl-2-acetoxymercuri -o-methylphenyliminothiazolid-4-one : (By applying first method). To the warm solution of 3-o-methylphenyl-2-o-methylphenyliminothiazolid-4-one (1 g.) dissolved in alcohol-acetic acid was added a solution of mercuric acetate (2·15 g.) in water acidified with acetic acid. The mixture was stirred well, no precipitation took place even after 1 hr. The mixture was then kept overnight, even then no precipitate appeared. It was then left for a week, after which a little precipitate separated. It was then diluted with excess of water and the precipitate obtained was purified as given under the first method. The compound was obtained in the form of a light yellow powder. Yield: 1·21 g. (40% of theory). turns orange near 176-78°C. and melts at 182-84°C. Found: Hg, 49·67. $C_{12}H_{20}N_2O_5SHg_2$ requires Hg, 49·34 per cent.

This experiment was repeated by taking the reactants in the same proportion as described above and the reaction mixture was refluxed directly on an asbestos wire-gauze (*as described under method second*). After two minutes of reflux the mixture turned light yellowish green. The refluxing was continued. After eight minutes the reaction mixture became turbid, indicating separation of the compound. After 20 minutes refluxing the rate of precipitation increased but the supernatant liquid was not colourless, so the refluxing was continued for 10 minutes more and the com-

TABLE 1

3-ACETOXYMERCURIARYL-2-ACETOXYMERCURIARYLIMINOTHIAZOLID-4-ONES
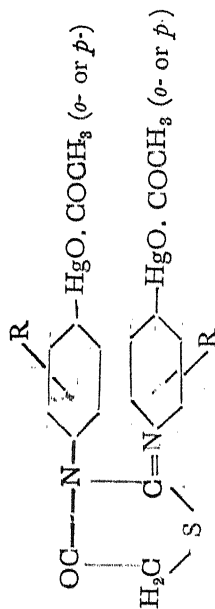
(R = CH_3 or Cl at o-, m- or p- positions with respect to N atoms)
T = corresponding 3-Aryl-2-aryliminothiazolid-4-one
M = Mercuric acetate

S. N.	Aryl group	Molecular formula	Constituents and acetic acid used	Yield (of theory)	M. P.	% of Mercury Found	Calc.
1.	m-Methylphenyl-	$C_{21}H_{20}N_2O_5SHg_2$	T (0·5 g)+M (1·1 g); 12 c. c.	52%	turns brown at 188° and melts at 200°C.	48·78	49·33
2.	o-Methylphenyl-	C_2 $H_{20}N_2O_5SHg_2$	T (1 g)+M (2·2 g); 20 c. c.	55%	darkens in colour at 199° and melts at 201-2°C.	50·07	49·33
3.	o-Chlorophenyl-	$C_{19}H_{14}Cl_2N_2O_5SHg_2$	T (0·25 g)+M (0·48 g); 10 c. c.	63%	turns brown at 175° and melts at 185°C.	47·40	46·96
4.	m-Chlorophenyl-	$C_{19}H_{14}Cl_2N_2O_5SHg_2$	T (0·25 g)+M (0·48 g); 10 c. e.	60%	darkens at 187-8° and melts at 196°C.	47·08	46·96
5.	p-Chlorophenyl-	$C_{19}H_{14}Cl_2N_2O_5SHg_2$	T (0·5 g)+M (0·954 g); 15 c. c.	71%	darkens in color at 200°, m. p. 275°C.	46·90	46·96

pound precipitated was purified as described under method first. It was obtained as a light yellow powder. Yield: 1·80 g. (68% of theory). The compound turned orange at 175° and melted at 182-1°C. Found: Hg, 49·51. $C_{21}H_{20}N_2O_5SHg_2$ requires Hg, 49·34 per cent.

A study of the yields in the above two experiments clearly shows that 3-acetoxymercuri - o-methylphenyl - 2-acetoxymercuri-o-methylphenyliminothiazolid-4-one is not completely formed in the cold condition. Because of considerable reduction in the time taken for the completion of reaction as well as good yield; all the diacetoxymercuri-derivatives were prepared by the *second method*. Their m. p., analytical data and other details are reported in Table 1.

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EFFECT OF ALLYL GROUP ON OPTICAL ROTATORY POWER IN DERIVATIVE'S OF REYCHLER'S ACID

By

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ABSTRACT

The Allylamine salts of D- and L-Camphor $- \beta -$ sulphonic acid have been prepared and characterised. Its optical rotatory power has been studied in water, methyl alcohol, ethyl alcohol, coloroform and pyridine. In each solvent it was found to exhibit simple dispersion in the visible region. When its rotatory power is compared with that of ammonium - D - or L - camphor $\beta -$ sulphonate in water, methyl alcohol and ethyl alcohol it is found that the effect of allyl group is to cause a decrease in rotatory power.

INTRODUCTION

The work of Betti[1], Rule and Smith[2] first pointed out that the polarity of the substituent group has an effect on the magnitued of the rotatory power. It was found that in general the replacement of hydrogen in an optically active compound by a positive substituent displaces the rotation in the opposite sense to that due to a negative substituent. It was pointed out by Singh *et al*[3] that generally a positive group exhibits an increase in rotation and a negative group a decrease in rotation.[4]

In this paper the authors have studied the optical rotatory power of D-and L-allylamino-camphor-β-sulphonate and have compared its value with that of corresponding ammonium salt of Reychler's acid with a view to find the effect of allyl group.

EXPRIMENTAL

Reychler's D-camphor-β-sulphonic acid was prepared from natural D-camphor essentially according to the method given by Reychler[5] and described earlier by one of us.[6]

L-camphor-β-sulphonic acid was prepared by the oxidation of L-isoborneol which gave L-camphor which was sulphonated to give the acid.

Allylamino-camphor--β-sulphonate

9·28g. of D-or-L-camphor-β-sulphonic acid was condensed with 2·28g, of allylamine in ethyl acetate medium. It was then recrystallised from a mixture of benzene and carbon-tetra-chloride. For D-salt: Yield = 8g; melting-point = 125 - 26°C; found: $S = 10·92\%$, $C_{10}H_{15}$ $OSO_3H.H_2N - CH_2 - CH = CH_2$ requires 11·07%. For L-salt: Yield = 8·4g.; melting point = 125 - 26°C; found: $S = 11·15\%$, $C_{10}H_{15}$ $OSO_3H.H_2N - CH_2 - CH = CH_2$ requires 11·07%.

The salts are white crystalline solid. They are highly solouble in water, methyl alcohol and ethyl alcohol; less so in chloroform and pyridine; sparingly in benzene and practically insoluble in acetone, ethyl acetate, carbon-tetra-chloride, ether and petroleum ether.

The rotatory power determinations were made in a 2 dcm. tube and the results are recorded in table 1.

TABLE 1

Rotatory power of D-and-L-Allylamino-Camphor-β-Sulphonate in different Solvents

Solvent	Water		Methly alcohol		Ethyl alcohol		Chloroform		Pyridine	
Calculated $[\alpha]\lambda$ = disperson equation	$\pm\dfrac{4\cdot326}{\lambda^2} - 0\cdot1204$		$\pm\dfrac{6\cdot684}{\lambda^2} - 0\cdot1141$		$\pm\dfrac{6\cdot714}{\lambda^2} - 0\cdot1190$		$\pm\dfrac{7\cdot101}{\lambda^2} - 0\cdot1180$		$\pm\dfrac{8\cdot986}{\lambda^2} - 0\cdot1064$	
$\lambda_0 =$	0·3469		0·3377		0·3449		0·3435		0·3261	
Temperature	11·5°C		0°C		11·5°C		11°C		11·5°C	
Optical isomer	D -	L -	D -	L -	D -	L -	D -	L -	D -	L -
Concentration in g./100 ml.	0·9904	0·9876	0·9786	0·9904	0·9868	0·9984	0·9724	0·9980	0·9928	0·9972
Wave length	Obs. $[\alpha]_\lambda$	Obs. $[\alpha]_\lambda$	Obs. $[\alpha]_\lambda$	Obs. $[\alpha]_\lambda$	Obs. $[\alpha]_\lambda$	Obs. $[\alpha]_\lambda$	Obs. $[\alpha]_\lambda$	Obs. $[\alpha]_\lambda$	Obs. α'_λ	Obs. $[\alpha'_\lambda$
Hg_{4358}	+63·10°	-63·28°	+88·39°	-87·33°	+94·75°	-94·15°	+98·72°	-97·19°	+106·26°	-106·28°
Li_{4603}	47·45	47·59	67·44	67·14	72·45	72·11	75·38	75·15	85·01	85·23
Cd_{4673}	44·42	44·55	63·86	63·61	67·89	67·63	70·44	70·14	78·55	78·72
Cu_{4800}	39·37	39·48	57·73	57·55	60·28	60·59	63·24	63·12	72·52	72·20
Cd_{5085}	31·30	31·38	46·49	46·44	48·13	48·07	50·13	50·60	59·42	58·66
Hg_{5461}	24·23	24·30	36·27	36·34	37·49	37·56	39·59	39·57	46·83	46·63
Hg_{5750}	20·19	20·25	30·14	30·29	31·41	31·04	32·90	33·06	39·78	39·60
Na_{5893}	19·18	19·23	26·61	28·77	29·38	29·54	30·85	31·06	37·29	37·10
Li_{6104}	17·16	17·21	26·05	25·74	26·34	25·54	28·28	28·05	33·44	34·09
Ne_{6402}	15·14	15·18	22·48	22·71	23·30	23·05	24·68	24·54	29·71	29·53
Cd_{6438}	14·64	14·68	21·97	22·21	23·60	23·53	24·16	24·04	29·21	29·03
Li_{6708}	13·12	13·16	19·42	19·63	20·26	20·53	21·59	21·54	26·13	26·05

	Shows no Mutarotation	Shows mutarotation after 22 hrs. for D-salt $[\alpha]^{37}_{5461} =$ +34·23° and for L-salt $-[\alpha]^{9°}_{5461} =$ −33·28°	Shows mutarotation for after 22½ hrs. for D-salt $[\alpha]^{11\cdot5}_{5461} =$ + 33·94° and for L-salt $-[\alpha]^{11\cdot5}_{4561} =$ − 33·55°	Shows mutarotation after 23 hrs. for D-salt $[\alpha]^{11}_{5461} =$ + 34·90° and for L-salt $-[\alpha]^{11}_{4561} =$ − 35·0°	Shows mutarotation after 23 hrs. for D-salt $[\alpha]^{115}_{5461} =$ + 38·75 and for L-salt $-\alpha^{115}_{5461} =$ −39·10°

TABLE 2

Comparison of Optical Rotatory Power of active ammonium-camphor-β-sulphonate and allylamino-camphor-β-sulphonate

Specific Rotation for wavelength (λ)	Water				Methyl alcohol				Ethyl alcohol			
	Ammonium Salt		Allylamine Salt		Ammonium Salt		Allylamine Salt		Ammonium Salt		Allylamine Salt	
	D—	L—	D—	L—	D—	L—	D—	L—	D—	L—	D—	L—
Hg$_{4358}$	+73·38°	−73·38°	+63·10°	−63·28°	+100·54°	−100·50°	+88·33°	−87·33°	+115·00°	−115·09°	+94·75°	−94·15°
Li$_{4603}$	54·78	−54·28	47·45	47·59	79·53	79·00	67·44	67·14	31·50	31·37	72·45	72·11
Cd$_{4678}$	50·76	50·26	44·42	44·55	74·52	74·00	63·86	63·61	85·00	85·56	67·89	67·60
Cd$_{4800}$	44·73	45·23	39·37	39·48	67·02	67·50	57·73	57·55	77·00	77·06	60·28	60·59
Cd$_{5086}$	35·18	36·18	31·30	31·38	54·52	54·00	46·49	46·44	62·00	62·04	48·13	48·07
Hg$_{5461}$	27·14	27·14	24·23	24·30	43·51	43·50	36·27	36·34	49·00	49·03	37·49	37·56
Hg$_{5780}$	22·61	22·61	20·19	20·25	36·51	37·00	30·14	30·29	41·00	40·53	31·41	31·04
Na$_{5893}$	21·10	21·10	19·18	19·23	34·51	34·50	28·61	28·77	39·00	38·53	29·38	21·54
Li$_{6104}$	18·59	18·09	17·16	17·21	31·51	31·50	26·05	25·74	35·00	35·02	26·34	26·54
Ne$_{6402}$	16·58	17·08	15·14	15·18	27·51	27·50	22·48	22·71	30·50	30·52	23·30	23·03
Cd$_{6438}$	16·08	16·58	14·64	14·68	27·01	27·00	21·97	22·21	30·00	30·02	22·80	22·53
Li$_{6708}$	14·57	14·57	13·12	13·16	24·50	24·50	19·92	19·68	27·00	26·52	20·26	20·53

The rotatory power given in Table I was analysed by the method of Lowry.[7] On plotting $1/[\alpha]$ against λ^2 a straight line was obtained in each case. This indicated that the compound shows simple dispersion and hence the rotation can be expressed by one term of Drude's equation. In each case the equation was calculated and is given in Table I. It was found that there is very good agreement between the observed values of rotation and those obtained from these calculated equations in the whole of the visible region of the spectrum.

DISCUSSION

The rotatory power of D- and L forms given in Table I supports Pasteur's Principle of Molecular Dissymmetry. In about 120 readings the difference between D-and L froms is seldom found to be beyond the exprimental error.

In case of non-ecqueous solvents such as methyl alcohol, ethyl alcohol, chloroform and pyridine the optically active allylamino-camhpor-β-sulphonate exhibit slight mutarotation after 22-23 hrs. This mutarotation is probably due to the very slow formation of ketimine as suggested by Schreiber and Shriner.[8]

The authors had previously studied the rotatory power of ammonium-D-or L-camphor-β-sulphonate in aqueous and non-aqueous solvents.[9] A comparision of its rotatory power with that of allyl amino-D- or L- camphor-β-sulphonate in water, ethyl alcohol and methly alcohol for 12 different wave lengths is given in Table 2.

From this table it is clear that in water, methyl alcohol and ethyl alcohol allylamino-D-or L-camphor-β-sulphonate exhibits a lower rotation as compared with ammonium-D-or L-camphor-β- sulphonate. The decrease in rotation is practically uniform in the whole of the visible region for the 12 wavelengths studied.

These results are in agreement with the view that substitution of an electronegative group in the place of electro-positive hydrogen causes generally a decrerse in rotation.

ACKNOWLEDGEMENT

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THERMALLY INDUCED CONVECTION IN A STELLAR ATMOSPHERE

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ABSTRACT

In the present note thermally induced convection in an atmosphere following the polytropic law $p \propto \rho^{\Gamma}$ is investigated. The atmosphere is supposed to be initially plane parallel. The density from the top to the bottom varies by a large factor as is found in the convective zone of the sun. The viscosity and heat conduction is ignored but radiation is taken into account. This is the main difference from the previous works. Perturbation theory is applied with the assumption that the perturbations are adiabatic and small. These perturbation equations are linearized. The integration is carried out for the fundamental mode. The thickness of the disturbed zone is found to be much larger than for the case when radiation was neglected. It is found that the integrations are possible for horizontal wave lengths much less than the thickness of the atmosphere.

INTRODUCTION

The study of thermally induced convection was first made by Lord Rayleigh (1916) for the case of a homogeneous incompressible fluid. The recent studies of miss Vitense (1953) of solar convective zone have shown that the depth of the zone is too large to apply this homogeneous theory. The varition of density from top to bottom is found to be at least of the order of 10^4. The various phenomena observed on the surface of the sun (granules, flares, etc.) seem to indicate that the convection in stars in general and in the sun in particular is turbulent in character. The theory of turbulence is not developed very much to follow the investigations in all its details. The mixing length theory which people generally relate to the scale heights does not seem to be quite sound. The relation between the two is not well known. Even the scale height itself in the case of these stellar convection zones varies from about 200 Km to about 20,000 Km. Therefore in the present investigation an attempt is made to find the scale of unstable convective zone for a compressible inviscid atmosphere in which the density and the scale of height varies appreciably and in which the energy carried by the radiation is also taken into account.

BASIC EQUATIONS AND APPROXIMATIONS

For conservation of momentum we have :

$$\begin{aligned}
\frac{\partial u}{\partial t} + u \frac{\partial u}{dx} + v \frac{du}{dy} - w \frac{\partial u}{\partial z} &= -\frac{1}{\rho} \frac{\partial p}{\partial x} \\
\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial}{\partial y} - w \frac{\partial v}{\partial z} &= -\frac{1}{\rho} \frac{\partial p}{\partial y} \\
\frac{\partial w}{\partial t} + u \frac{\partial w}{\partial x} + v \frac{\partial w}{\partial z} - w \frac{\partial w}{\partial z} &= -g + \frac{1}{\rho} \frac{\partial p}{\partial z}
\end{aligned} \right\} \quad \dots (1)$$

It may be noted here that the positive direction of the z-axis is taken downwards towards the centre of the star and origin at the surface of the star. Thus the

positive direction of w, outward radial component of the velocity is towards the negative z axis.

Conservation of mass gives

$$\frac{\partial \rho}{\partial t} + u\frac{\partial \rho}{\partial x} + v\frac{\partial \rho}{\partial y} - w\frac{\partial \rho}{\partial z} + \rho\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} - \frac{\partial w}{\partial z}\right) = 0 \quad \ldots\ldots\ldots(2)$$

Conversation of energy leads to

$$\frac{\partial p}{\partial t} + u\frac{\partial p}{\partial x} + v\frac{\partial p}{\partial y} - w\frac{\partial p}{\partial z} = \frac{\gamma p}{\rho}\left[\frac{\partial \rho}{\partial t} + u\frac{\partial \rho}{\partial x} + v\frac{\partial \rho}{\partial y} - w\frac{\partial \rho}{\partial z}\right] - (\gamma-1)\,\text{div}\,\vec{F}. \quad \ldots(3)$$

where F is the radiative flux and other symboles have their usual meaning. F is given by the following relation.

$$F = -\frac{4ac}{3}\cdot\frac{T^3}{k\rho}\,\text{grad}\,T \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

In actual case it is this expression for radiative flux which makes the problem most complicated is the actual expression for k, which itself is quite complicated is taken in this equation. However, to avoid the mathematical complications the prolem is solved in a crude approximation by assuming that the total continuous absorption per unit volume is proportional to the cube of temperature. This assumption implies that the radiative flux is proportional to the temperature gradient. With this simplifying assumption when we substitue (4) in (3) we get

$$\frac{\partial p}{\partial t} + u\frac{\partial p}{\partial x} + v\frac{\partial p}{\partial y} - w\frac{\partial p}{\partial z} = \frac{\gamma p}{\rho}\left[\frac{\partial \rho}{\partial t} + u\frac{\partial \rho}{\partial x} + v\frac{\partial \rho}{\partial y} - w\frac{\partial \rho}{\partial z}\right]$$

$$+ (\gamma-1)\,K\left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right]\ldots\ldots\ldots(5)$$

where

$$K = \frac{4ac}{3}\cdot\frac{T^3}{k\rho}.$$

The last equation holds only under the condition that heat transfer is by radiation and convection alone. Heat exchanges by conduction are negligible. This assumption is quite justified for any gaseous material which is not degenerate. In particular so far as stellar atmosphere is concerned the dominating conveyance for carrying the flux is radiation in general and convection becomes important contributor in some special circumstances.

To get the distribution of the physical variables we can still simplify the problem by assuming a plane parallel atmosphere. This assumption can be justified for the particular cases where the thickness of an stellar atmosphere is so small in comparission with the stellar radius that we can neglect the curvature changes for the whole extent of the atomsphere. In such cases we can also take the acceleration due to gravity as constant and it is certainly directed towards the centre of the star that is in the positive direction of our z axis.

The equations of the zeroth order are

$$\rho_0 \frac{\partial u}{\partial t} = -\frac{\partial p_0}{\partial x} = 0$$

$$\rho_0 \frac{\partial v}{\partial t} = -\frac{\partial p_0}{\partial y} = 0$$

$$\rho_0 \frac{\partial w}{\partial t} = -g\,\rho_0 + \frac{\partial p_0}{\partial z} = 0 \qquad\qquad \left.\right\} \qquad\qquad \dots\dots\dots\dots\dots(6)$$

$$\frac{\partial^2 T_0}{\partial z^2} = 0$$

Here we have taken that initially the atmosphere is in hydrostatic equilibrium at rest. If this atmosphere obeys the following polytropic law for density and pressure relation

$$p_0 \,\alpha\, \rho_0{}^{\Gamma} \qquad\qquad \dots\dots\dots\dots\dots\dots\dots\dots . (7)$$

we get the equilibrium values from the solutions of the equations (6) in the following form :

$$p_0 = \frac{\Gamma-1}{\Gamma} g\,A\, z^{\frac{\Gamma}{\Gamma-1}}$$

$$\rho_0 = A\, z^{\frac{1}{\Gamma-1}} \qquad\qquad \left.\right\} \qquad\qquad \dots\dots\dots\dots\dots(8)$$

$$T_0 = \frac{\Gamma-1}{\Gamma}\left(\frac{\mu H}{k}\right) gz$$

In deriving these values in equations (8) we have used the general equation of state

$$\frac{p_0}{\rho_0 T_0} = \frac{k}{\mu H}$$

where μ is the mean molecular weight, k is the Boltzmann constant, H is the weight in grams of hydrogen alone or to be more accurate it is the atomic weight unit expressed in grams. A is constant, g is the acceleration due to stellar gravity.

Now we assume a small perturbations imposed on these equilibrium state values and derive the equations which govern the perturbations. We denote the difference between a quantity in perturbed state and its value in equilibrium state by the symbol with a subscript 1. Thus we substitute in the equations of the problem the values

$$p = p_0 + p_1, \quad \rho = \rho_0 + \rho_1, \quad T = T_0 + T_1$$
$$u = u_0 + u_1, \quad v = v_0 + v_1, \quad w = w_0 + w_1$$

and make use of the equilibrium state equations (6). If we assume the quantities p_1, ρ_1, T_1, u_1, v_1, and w_1 to be small of the first order and neglect the terms of the

second and higher orders, we arrive at the following perturbation equations

$$\rho_0 \frac{\partial u_1}{\partial t} = -\frac{\partial p_1}{\partial x} \qquad \cdots \qquad \cdots \qquad \cdots \quad (9)$$

$$\rho_0 \frac{\partial v_1}{\partial t} = -\frac{\partial p_1}{\partial y} \qquad \cdots \qquad \cdots \qquad \cdots \quad (10)$$

$$\rho_0 \frac{\partial w_1}{\partial t} = -g\rho_0 + \frac{p_1}{\partial z} \cdots \qquad \cdots \qquad \cdots \quad (11)$$

$$\frac{\partial \rho_1}{\partial t} + \frac{\partial}{\partial x}\Big(\rho_0 u_1\Big) + \frac{\partial}{\partial y}\Big(\rho_0 v_1\Big) - \frac{\partial}{\partial z}\Big(\rho_0 w_1\Big) = 0 \ \cdots \qquad \cdots \quad (12)$$

$$\frac{\partial p_1}{\partial t} = \frac{\gamma p_0}{\rho_0} \cdot \frac{\partial \rho_1}{\partial t} + \Big[\frac{\partial p_0}{\partial z} - \frac{\gamma p_0}{\rho_0} \cdot \frac{\partial \rho_0}{\partial z}\Big]w_1$$

$$+ (\gamma - 1)\,K\Big[\frac{\partial^2 T_1}{\partial x^2} + \frac{\partial^2 T_1}{\partial y^2} + \frac{\partial^2 T_1}{\partial z^2}\Big] \qquad \cdots \quad (13)$$

CHARACTERISTIC EQUATIONS

To get the solution of this system of differential equations we substitute the following

$$u_1 = u^* \, e^{\,i\,(lx + my) + \sigma t}$$

$$v_1 = v^* \, e^{\,i\,(lx + my) + \sigma t}$$

$$w_1 = \frac{g}{\sigma} w^* \, e^{i(lx + my) + \sigma t}$$

$$p_1 = \Big(gA/k_1{}^{\frac{\Gamma}{\Gamma - 1}}\Big)_r {}^{\frac{1}{\Gamma - 1}} p^* \, e^{\,i\,(lx + my) + \sigma t}$$

$$T_1 = \Big(g/k_1\Big)\Big(\frac{\mu H}{k}\Big)T^* \, e^{\,i\,(lx + my) + \sigma t}$$

$$\rho_1 = \Big(A/h_1{}^{\frac{1}{\Gamma - 1}}\Big)\rho^* \, e^{\,i\,(lx + my) + \sigma t}$$

$$\cdots\cdots\cdots\cdots (14)$$

Here the starred quantities are functions of z alone, l and m have their usual meaning and are related to the horizontal wave length, σ is the e-folding frequency. k_1, r and e are the non-dimensional quantities which are substituted to simplify the integration. These are defined as follows:

$$r = k_1 z, \quad l^2 + m^2 = k_1{}^2, \quad e^2 = \sigma_2/k_1 z \ \cdots \qquad \cdots \qquad \cdots \quad (15)$$

With these substitution the equations (9)—(13) after few eliminations and simplifications reduce to the following:

$$\frac{dp^*}{dr} = \frac{p^*}{r} + w^* - \frac{\Gamma}{\Gamma - 1} \cdot \frac{T^*}{r} \qquad \cdots \qquad \cdots \qquad \cdots (16)$$

[112]

$$\frac{dw^*}{dr} = \left[\frac{\Gamma}{\Gamma-1} \cdot \frac{e^2}{r} + 1\right]p^* - \frac{1}{\Gamma-1} \cdot \frac{w^*}{r} - \frac{\Gamma}{\Gamma-1} \cdot \zeta^2 \frac{T^*}{r} \qquad \dots(17)$$

$$\frac{d^2T^*}{dr^2} = T^* + C\, r^{\frac{1}{\Gamma-1}}\left[p^* + \left(1 - \frac{\gamma}{\Gamma}\right)\frac{1}{\gamma-1} \cdot \frac{w^*}{\zeta^2} - \frac{\gamma}{\gamma-1}\, T^*\right] \qquad (18)$$

where
$$C \equiv \left(\frac{k}{\mu H}\right) \cdot \left(\sigma A/K\, k_1^{2+\frac{1}{\Gamma-1}}\right) \qquad \dots \qquad \dots (19)$$

BOUNDARY CONDITIONS

Following boundary conditions are required to be satisfied by the solutions of these equations.

$$\left.\begin{array}{l} \rho_0 w_1 = 0 \text{ at the surface } r = 0 \\ \text{and also } \rho_0 w_1 = 0 \text{ at the bottom } r = r_0 = k_1 z_0 \end{array}\right\} \quad \dots(20)$$

First of these conditions is satisfied by requiring the kinetic energy to be finite at the surface. These two boundary conditions are not enough to specify the problem. Thus we are still left with two degrees of freedom to be specified later.

ESTIMATION OF CONSTANT 'C'

To obtain an estimation of the constant C following procedure is adopted.

From equation (4) we have

$$K = -\frac{F}{\text{grad } T} = (L/4\,\pi\, R^2) \cdot 1/\frac{dT}{dz}) \qquad \dots \qquad \dots (21)$$

substituting this in equation (19) we get

$$C = \left(A/k_1^{1\cdot 5 + \frac{1}{\Gamma-1}}\right)\zeta^{g} \cdot \frac{\Gamma-1}{\Gamma}\left(4\,\pi\, R^2/L\right) \qquad \dots (22)$$

In arriving at the last expression we have replaced σ by ζ and the value of $\frac{dT}{dz}$ is taken from the equilibrium values. The constant A is obtained from the following equation in terms of the equilibrium values.

$$\log A = \log p_0 + \frac{1}{\Gamma-1}\log \frac{\Gamma-1}{\Gamma} + \frac{1}{\Gamma-1}\log g + \frac{\Gamma}{\Gamma-1}\log\left(\frac{\mu H}{k}\right) - \frac{\Gamma}{\Gamma-1}\log T_0$$
$$\dots (23)$$

The value $\Gamma = \frac{20}{11}$ was chosen following Skumanich (1955). In his investigation the energy changes by processes other than convection were neglected. For the purpose of equation (23) the values of p_0 and T_0 were taken from the model atmosphere by Swihart (1956). For this estimation his second and sixth models were used taking the values of p_0 and T_0 at certain representative points at the optical depth 2.

From the observations of granules on the photosphere of the sun some estimate was made for the horizontal half wave length. Using all this information one can

get some reasonable estimate of the value of constant C as 0·03 for $\gamma = 5/3$.

These values of $\Gamma = \dfrac{20}{11}$ and $\gamma = 5/3$ give r, the measure of the degree of instability, as follows :

$$r = \frac{(d\,T_0/dz)_{true} - (d\,T_0/dz)_{ad}}{(d\,T_0/dz)_{ad}} \qquad \qquad \ldots(24)$$

$$= \left(1 - \frac{\gamma}{\Gamma}\right)\bigg/ (\gamma - 1)$$

$$= \frac{1}{8}$$

STARTING VALUES

It may be noted that the coefficients of the differential equations are not regular at the surface $r = 0$. Therefore the actual integration has to be started from a suitable but very small value of r. For these starting values of the variables following series in terms of the powers of r for p^* and similar series for w^+ and T^+ were substituted.

$$
\begin{aligned}
p^* = {}& [p_{00} + p_{01}r + p_{02}r^2 + p_{03}r^3 + \ldots\ldots) + \log r\,(p_{00}' + p_{01}'r + p_{02}'r^2 + \\
& \hspace{8cm} p_{03}'r^3 + \ldots\ldots)] \\
& + S[(p_{10} + p_{11}r + p_{12}r^2 + p_{13}r^3 + \ldots\ldots) + \log r\,(p_{10}' + p_{11}'r + p_{12}'r^2 + \\
& \hspace{8cm} p_{13}'r^3 + \ldots\ldots)] \\
& + S^2[\,(p_{20} + pr_{21} + p_{22}r^2 + p_{23}r^3 + \ldots\ldots) + \log r\,(p_{20}' + p_{21}'r + p_{22}'r^2 \\
& \hspace{8cm} + p_{23}'r^3 + \ldots\ldots)] \\
& + \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \quad (25) \\
& \quad \ldots \qquad \ldots \qquad \ldots \qquad \ldots
\end{aligned}
$$

where

$$S = r^{\frac{1}{\Gamma - 1}}$$

We have noted before that the boundary conditions of the problem can only evaluate two out of four arbitrary constants of integration in the general solution. The other two are at our disposal and can be chosen arbitrarily to suite our numerical facilities. Actually two integrations are performed numerically one with $p_{01} = 0$ and the other with $T_{01} = 0$. These solutions, here after in this text, are called P — solution and T — solution respectively. For these two integrations the starting values were obtained from the following series at the point $r = 0·01$
For T — solution

$$T^* = r\left(1 + \frac{r^2}{3\,1} + \frac{}{5\ 1} + \ldots\ldots\right) + C\,S\,r^3\,\frac{(\Gamma - 1)^2}{(3\,\Gamma - 2)\,(2\,\Gamma - 1)} \times$$

$$\left[\frac{\Gamma\,(5\,\Gamma - 3)}{(3\,\Gamma - 2)\,(2\,\Gamma - 1)}\left\{1 + \left(1 - \frac{\gamma}{\Gamma}\right)\frac{1}{\gamma - 1}\right\} - \frac{\gamma}{\gamma - 1}\right] + \ldots\ldots\ldots$$

$$- C\,S\,r^3 \log r\,\left[\frac{\Gamma\,(\Gamma - 1)}{(3\,\Gamma - 2)\,(2\,\Gamma - 1)}\left\{1 + \left(1 - \frac{\gamma}{\Gamma}\right)\frac{1}{\gamma - 1}\right\} + \ldots\right]\ldots\ldots(26)$$

$$P^* = r^2\left[\frac{\Gamma}{\Gamma-1}\zeta^2 + \left\{\frac{1}{4}\cdot\frac{\dot{\Gamma}}{2\Gamma-1} + \frac{1}{2}\cdot\frac{\Gamma(\Gamma-1)}{(2\Gamma-1)^2} - \frac{1}{6}\cdot\frac{\dot{\Gamma}}{\Gamma-1} + \tau^4\left(\frac{1}{2}\cdot\frac{\Gamma^2}{(2\Gamma-1)^2}\right.\right.\right.$$

$$\left.\left.\left. + \frac{3}{4}\cdot\frac{\Gamma^2}{(\Gamma-1)(2\Gamma-1)}\right)\right\}r + \ldots\ldots\right] - r\log r\left[\frac{\Gamma}{\Gamma-1} + \zeta^2\frac{\Gamma}{\Gamma-1}r + \right.$$

$$\left.\frac{1}{2}\left(\frac{\Gamma}{2\Gamma-1} + \tau^4\frac{\Gamma^2}{(2\Gamma-1)(\Gamma-1)}\right)r^2 + \ldots\right] + \text{CS}\,r^3\times$$

$$\left[-\frac{\Gamma^2(\Gamma-1)^2}{(2\Gamma-1)^3(3\Gamma-2)}\left\{1 + \left(1-\frac{\gamma}{\Gamma}\right)\frac{1}{\gamma-1}\right\} + \frac{\Gamma(\Gamma-1)^2}{(3\Gamma-2)(2\Gamma-1)^2}\left\{\frac{\Gamma(5\Gamma-3)}{(3\Gamma-2)(2\Gamma-1)}\times\right.\right.$$

$$\left.\left.\left(1 + \overline{1-\frac{\gamma}{\Gamma}}\cdot\frac{1}{\gamma-1}\right) - \frac{\gamma}{\gamma-1}\right\} + \ldots\ldots\ldots + \log r\cdot\frac{\Gamma^2(\Gamma-1)}{(2\Gamma-1)^2(3\Gamma-2)}\times\right.$$

$$\left.\left\{1 + \left(1-\frac{\gamma}{\Gamma}\right)\frac{1}{\gamma-1}\right\} + \ldots\ldots\ldots\ldots\right]\ldots\ldots\,(27)$$

$$w^* = r^2\left[\left\{\frac{\Gamma(\Gamma-1)}{(2\Gamma-1)^2} + \tau^4\left(\frac{\Gamma^2}{(2\Gamma-1)^2} + \frac{\Gamma^2}{(\Gamma-1)(2\Gamma-1)}\right)\right\} + \left\{\zeta^2\left(\frac{\Gamma(\Gamma-1)}{(3\Gamma-2)^2} + \frac{1}{2}\cdot\right.\right.\right.$$

$$\frac{\Gamma^2(\Gamma-1)}{(3\Gamma-2)^2(2\Gamma-1)}$$

$$\left. + \frac{5}{6}\frac{\Gamma}{(3\Gamma-2)} + \frac{1}{4}\cdot\frac{\Gamma^2}{(3\Gamma-2)(2\Gamma-1)} + \frac{1}{2}\cdot\frac{\Gamma^2(\Gamma-1)}{(3\Gamma-2)(2\Gamma-1)^2}\right) + \zeta^6$$

$$\left.\frac{1}{2}\cdot\frac{\Gamma^3}{(3\Gamma-2)^2(2\Gamma-1)} + \frac{3}{4}\cdot\frac{\Gamma^3}{(3\Gamma-2)(2\Gamma-1)(\Gamma-1)} + \frac{\Gamma^2}{(3\Gamma-2)(2\Gamma-1)^2}\right)\Big\}r + \ldots\right]$$

$$- r\log r\left[\zeta^2\frac{\Gamma}{\Gamma-1} + \left(\frac{\Gamma}{2\Gamma-1} + \frac{\tau^4\Gamma^2}{(2\Gamma-1)(\Gamma-1)}\right)r + \left\{\zeta^2\left(\frac{\Gamma}{3\Gamma-2} + \frac{1}{2}\cdot\right.\right.\right.$$

$$\left.\frac{\Gamma^2}{(3\Gamma-2)(2\Gamma-1)}\right) + \frac{\tau^6}{2}\cdot\frac{\Gamma^3}{(3\Gamma-2)(2\Gamma-1)(\Gamma-1)}\Big\}r^2 + \ldots\ldots\ldots\right] + \text{CS}\,r^3\times$$

$$\left[\frac{\Gamma(\Gamma-1)^2}{(3\Gamma-1)(3\Gamma-2)(2\Gamma-1)}\left\{\frac{\Gamma(5\Gamma-3)}{(3\Gamma-2)(2\Gamma-1)}\left(1+\overline{1-\frac{\gamma}{\Gamma}}\cdot\frac{1}{\gamma-1}\right) - \frac{\gamma}{\gamma-1}\right\}\right.$$

$$-\zeta^2\frac{\Gamma^2(\Gamma-1)^2}{(3\Gamma-1)(3\Gamma-2)(2\Gamma-1)^2}\left(1 + \overline{1-\frac{\gamma}{\Gamma}}\cdot\frac{1}{\gamma-1}\right) - \frac{\Gamma^2(\Gamma-1)^2\tau^2}{(3\Gamma-2)(3\Gamma-1)(2\Gamma-1)^2}\times$$

$$\left\{\frac{\Gamma(5\Gamma-3)}{(3\Gamma-2)(2\Gamma-1)}\left(1+\overline{1-\frac{\gamma}{\Gamma}}\cdot\frac{1}{\gamma-1}\right) - \frac{\gamma}{\gamma-1}\right\} - \frac{\Gamma^3(\Gamma-1)^2\tau^2}{(2\Gamma-1)^3(3\Gamma-2)(3\Gamma-1)}\times$$

$$\left\{1 + \left(1-\frac{\gamma}{\Gamma}\right)\frac{1}{\gamma-1}\right\} + \ldots\quad\ldots\quad\ldots\quad\ldots\quad\ldots\quad\ldots\quad\ldots + \text{CS}\,r^3\log r\times$$

$$\left[\frac{\tau^2\Gamma^2(\Gamma-1)}{(3\Gamma-2)(2\Gamma-1)^2}\left\{1 + \left(1-\frac{\gamma}{\Gamma}\right)\frac{1}{\gamma-1}\right\} + \ldots\quad\ldots\quad\ldots\quad\ldots\quad\ldots\right]$$

$$+\quad\ldots\quad\ldots\quad\ldots\quad\ldots\quad\ldots\quad\ldots\quad\ldots\quad\ldots\quad\ldots\quad(28)$$

For P—Solution :

$$p^* = r \left[1 + \zeta^{2r} + \frac{1}{2} \cdot \left(2\frac{\Gamma-1}{\Gamma-1} + \zeta^4 \, 2\frac{\Gamma}{\Gamma-1} \right) r^2 + \ \ldots \ \ldots \ \ldots \right]$$

$$- C S \, r^3 \left[\frac{\Gamma(\Gamma-1)^2}{(2\,\Gamma-1)^2(3\,\Gamma-2)} \left\{ 1 + (1 - \frac{\gamma}{\Gamma}) \frac{1}{\gamma-1} \right\} + \ \ldots \ \ldots \right]$$

$$+ \ \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (29)$$

$$T^* = C S \, r^3 \left[\frac{(\Gamma-2)^2}{(3\,\Gamma-2)(2\,\Gamma-1)} \left\{ 1 + (1 - \frac{\gamma}{\Gamma}) \frac{1}{\gamma-1} \right\} + \ \ldots \ \ldots \right]$$

$$+ \ \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (30)$$

$$w^* = r \left[\zeta^2 + \left(\frac{\Gamma-1}{2\,\Gamma-1} + \frac{\zeta^4}{2}\frac{\Gamma}{\Gamma-1} \right) r + \left\{ \zeta^2 \left(\frac{\Gamma-1}{3\,\Gamma-2} + \frac{1}{2} \cdot \frac{\Gamma(\Gamma-1)}{(3\,\Gamma-2)(2\,\Gamma-1)} \right) \right. \right.$$

$$\left. \left. + \frac{\zeta^6}{2} \cdot \frac{\Gamma^2}{(3\,\Gamma-2)(2\,\Gamma-1)} \right\} r^2 + \ \ldots \quad \ldots \quad \ldots \right]$$

$$+ CS \, r^3 \left[\frac{\Gamma(\Gamma-1)^2}{(3\,\Gamma-2)(3\,\Gamma-1)(2\,\Gamma-1)} \left(1 - \frac{\zeta^2\,\Gamma}{(2\,\Gamma-1)} \right) \left\{ 1 + (1 - \frac{\gamma}{\Gamma}) \frac{1}{\gamma-1} \right\} \right.$$

$$+ \ \ldots \quad \ldots \quad \ldots \quad \ldots \quad \quad + \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (31)$$

INTEGRATION

With these starting values the equations can be integrated numerically step by step. The general solution is given by

$$T\text{—solution} + B \times P\text{—solution}$$

where B is an arbitrary constant. This constant was obtained from the condition that at the lower boundary we have

$$w^*_T + B \, w^*_P = 0$$

and also

$$T^*_T + B \, T^*_P = 0 \qquad \left. \right\} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (32)$$

That is, the two integrations were terminated at the point where the two ratios w^*_T / w^*_P and T^*_P / T^*_T where equal. In general one can follow any one of the following two ways. Either one can specify the depth of the zone of perturbation r_0 and by trial and error hunt for the eigen value of ϱ which will specify the horizontal wave length or one can specify ϱ and wherever the conditions (32) are satisfied the integrations are terminated. Thus the value of r_0 which is related to the depth of the disturbed zone is obtained by a single integration alone.

For the present work the latter procedure was adopted. The numerical integrations was performed by hand with the help of desk calculater.

CONCLUSION

For the present integration ϱ is taken as 0·16. It is found that the vertical depth of the unstable zone is about twice the horigontal wave length. In

Rayleigh's study of incompressible homogenous atmosphere the eigen value for the fundamental mode, which is most unstable, is given by the relation

$$\frac{n^2 \, z_0}{g} = \alpha \, \beta^1 \, z_0 \left(\frac{k_1^2 \, z_0^2}{k_1^2 \, z_0^2 + \pi^2} \right) \tag{33}$$

where n is the e-folding frequency, z_0 is the depth of unstable zone, k_1 is the horizontal wave number. Following Skumanich, the coefficient $\alpha \, \beta^1 z_0$ can be transfered in terms of the present variables by comparing the system of perturbation equations and it can be evaluated using average temperature of polytropic atmosphere taking $\frac{1}{2} z_0$ as the representative value of z and present values of γ and Γ.

Therefore we can calculate $\frac{n^2 z_0}{g}$ knowing $k_1 \, z_0 = r_0$. For this integration it is found that

$$\frac{n^2 z_0}{g} = 0 \cdot 34 \text{ and } r_0 = 13 \cdot 3$$

On comparing this result with the rate of instability of the fundamental mode for the polytropic atmosphere of Skumanich and honogeneous atmosphere of Rayleigh it is found that the effect of inclusion of radiative energy transport is to move the corresponding point from the Skumanich's curve towards the Rayleigh's curve. This result should be treated with certain reservation because of the very approximate nature of the present work. Probably the tendency is correct. More and accurate integrations are necessary to decide this point. Definite improvements are necessary in terms of the opacity formula which is treated in the present work with wild approximation.

The author wishes to express his gratitude to Dr. M. Schwarzschild for suggesting this problem and many valuable discussions in the initial stage of the problem.

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THE INFLUENCE OF THE CONCENTRATION OF THE GELATING
MATERIAL ON THE GELLING TIME OF SOME SUCCINATE GELS : PART I

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ABSTRACT

The equation $1/kc^2t + 1/c =$ constant, where c and t are the concentration of the substance undergoing gelation and the gelling time, respectively, and k is a constant, has been tested during the formation of aluminium and ferric succinate gels. Mechanism of gel formation as revealed by the above investigations has been discussed.

Several emperical relations (1, 2, 3) have been placed in literature correlating the gelling time and the concentration of the gelating particles. It is also reported by several workers that gelation and coagulation are closely interrelated (4). That, the fall in electric charge to a critical value is sufficient for agglomeration of particles for coagulation, as observed by Powis (5), is also true for gelation. The hydration of the colloidal surface leads to sufficient stability of the colloidal particles, because the aggregation linkage across the layer of the liquid medium is necessarily weak (6). Coalescence therefore would either require the removal of the adsorbed layer of the solvent on the colloid surface or aggregation occurs at spots on the surface which is of least lyophilic nature. If the area of this region is large, compact aggregation occurs at small number of spots which will, therefore, be sufficiently loose and may lead to the formation of a network structure which according to Freundlich (7) is a typical feature of, gel formation. With these ideas in view Ghosh and associates (8) in a recent communication, derived a concentration-time relation for gelation from the well known Smoluchowski's equation for coagulation of sols. The relation is :

$$1/kc^2t + 1/c = \text{const} \dots \dots \dots \dots \dots (1)$$

where c is the concentration of the reacting substances yielding the gel, t the gelling time and k is given by $4\pi DR$. D being the diffusion constant and R the distance between the two particles at which a lasting contact is made.

In this paper, we are recording our experimental results with ferric and aluminium succinate gels in support of the equation derived by Ghosh and associates. The gels investigated are new in literature and have been prepared in these laboratories for the first time (9,10).

EXPERIMENTAL

The gelation has been carried out by the metathesis of sodium succinate and excess of ferric chloride or aluminium chloride solutions of suitable concentrations. When sodium succinate is gradually added, say, to a ferric chloride solution, the precipitate of ferric succinate first formed gets peptised when the former is in small amount. If the addition of sodium succinate is continued, there comes a region where either a gelatinous precipitate or a transparent gel separates out. In preliminary experiments it has been noted that a suitable concentration of the reacting solutions must be chosen to yield a transparent gel.

Equal volumes of solutions of the chloride of iron or aluminium and of sodium succinate of suitable concentrations are taken in gradually decreasing quantities to produce different amounts of metal succinates in the system. As the amount of sodium chloride produced by the interaction will decrease with the decreasing quantities of the chloride and sodium succinate, calculated amount of this salt is introduced in the mixtures. The gelling time is noted at $32 \pm 0.1°C$, by the method described by Bose and Mushran (11).

In Tables 1 to 7 are presented our results on the gelation of ferric and aluminium succinate by metathetical processes. In column 1 is indicated the amounts of the chlorides of iron or aluminium and of sodium succinate of known strengths in gradually decreasing quantities to produce different amounts of metal succinate and in column 2 is indicated the amount of sodium chloride introduced in such mixtures. In the last two columns are recorded the values of $1/c$ and $1/c^2t$ where c and t have their usual meanings.

TABLE 1

Total Volume = 10.0 ml.

3N/5 FeCl$_3$ and 0.54 N Sod. Succinate (equal amount each)	0.54 N NaCl	Gelling time	$1/c$	$1/c^2t$
1.0	0.0	4.5	1.000	0.222
0.8	0.2	5.0	1.250	0.313
0.6	0.4	5.75	1.667	0.434
0.4 (ml)	0.6 (ml)	7.5 (mins)	2.500	0.767

TABLE 2

Total Volume = 10.0 ml.

3N/10 FeCl$_3$ and 0.51 N Sod. Succinate (equal amount each)	0.51 N NaCl	Gelling time	$1/c$	$1/c^2t$
1.0	0.0	6.25	1.000	0.160
0.8	0.2	9.0	1.250	0.173
0.6	0.4	13.0	1.667	0.214
0.4 (ml)	0.6 (ml)	21.0 (mins)	2.500	0.298

TABLE 3
Total Volume = 10·0 ml.

3N/5 FeCl$_3$ and 0·48 N Sod. Succinate (equal amount each)	0·48 N NaCl	Gelling time	$1/c$	$1/c^2t$
1·0	0·0	11·5	1·000	0·087
0·8	0·2	14·5	1·250	0·108
0·6	0·4	21·0	1·667	0·132
0·4 (ml)	0·6 (ml)	30·0 (mins)	2·500	0·209

TABLE 4
Total Volume = 9·0 ml.

3N/5 AlCl$_3$ and 0·54 N Sod. Succinate (equal amount each)	0·54 N NaCl	Gelling time	$1/c$	$1/c^2t$
3·0	0·0	7·0	0·333	0·0159
2·5	0·5	8·5	0·400	0·0188
2·0	1·0	10·5	0·500	0·0238
1·5 (ml)	1·5 (ml)	14·0 (mins)	0·666	0·0317

TABLE 5
Total Volume = 9·0 ml.

3N/5 AlCl$_3$ and 0·555N Sod. Succinate (equal amount each)	0·555N NaCl	Gelling time	$1/c$	$1/c^2t$
3·0	0·0	4·0	0·333	0·0278
2·5	0·5	4·5	0·400	0·0356
2·0	1·0	5·5	0·500	0·0454
1·5 (ml)	1·5 (ml)	7·0 (mins)	0·666	0·0634

TABLE 6

Total Volume $= 9\cdot0$ ml.

3N/5 AlCl$_3$ and 0·525N Sod. Succinate (equal amount each)	0·525N NaCl	Gelling time	$1/c$	$1/c^2t$
3·0	0·0	8·5	0·333	0·0131
2·5	0·5	11·25	0·400	0·0142
2·0	1·0	16·0	0·500	0·0156
1·5 (ml)	1·5 (lm)	25·0 (mins)	0·666	0·0178

TABLE 7

Total Volume $= 9\cdot0$ ml.

3N/5 AlCl$_3$ and 0·51N Sod. Succinate (equal amount each)	0·51N NaCl	Gelling time	$1/c$	$1/c^2t$
3·0	0·0	25·0	0·333	0·0044
2 5	0·5	35·0	0·400	0·00459
2·0	1·0	45·0	0·500	0·00555
1·5 (ml)	1·5 (ml)	65·0 (mins)	0·666	0·00684

The values of $1/c$ and $1/c^2t$ are plotted in fig. 1 and 2. It is seen that straight lines are obtained, establishing the validity of equation (1), both in the case of ferric succinate and aluminium succinate gels.

FIG.1 $\frac{1}{c^2t}$ versus $\frac{1}{c}$

C in ml., Sod. Succ. :—·54N,-o-o-; 51N, -x-x-; ·48N,-o-o-, with equal amount of 3N/5, Fe Cl$_3$

FIG. 2. $\frac{1}{c^2t}$ versus $\frac{1}{c}$

C in ml., Na- Succ. :-·555N, -x-x- ; ·540N, -o-o-; ·525N, -△-△-, ·510N,-o-o-. with equal amount of 3N/5, AlCl$_3$.
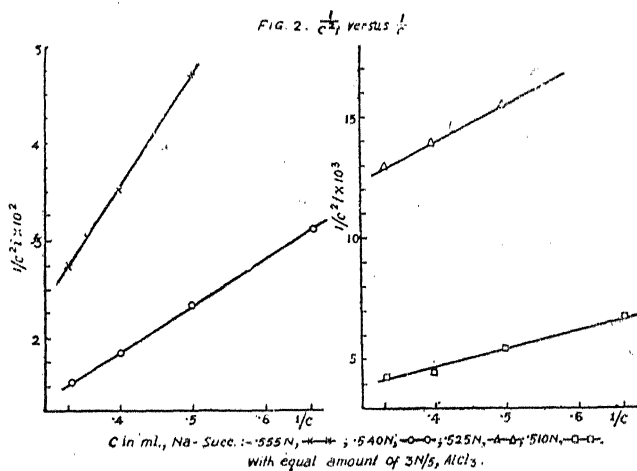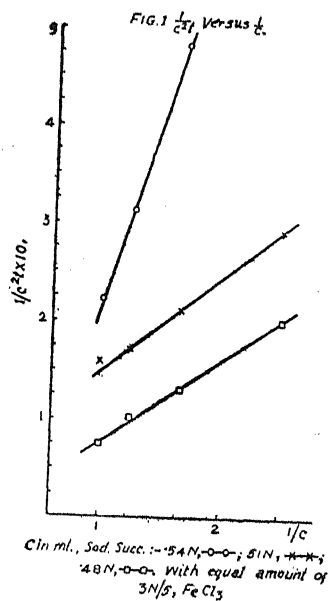
It is shown in Part II of this series, that, freshly precipitated ferric succinate can be easily peptised by succinic acid and a clear sol of ferric succinate can thereby be obtained. This sol is sensitive to electrolytes and yields transparent gels. From the experimental data presented in Part II tables 8 and 9 are compiled for the gelling time of sols of different concentrations with the same amount of electrolyte, both sodium chloride and potassium sulphate.

TABLE 8

N NaCl (ml)	Values of $1/c^2t$ for		
	$1/c = 0.250$	$1/c = 0.375$	$1/c = 0.500$
Sol A :			
0·4	0·00312	0·01082	0·02000
0·3	0·00208	0·00670	0·01388
0·2	0·00089	0·00350	0·00748
Sol B :			
0·4	0·00250	0·00586	0·01136
Sol C :			
0·8	0·00694	0·00879	0·01400
0·6	0·00250	0·00500	0·00862

This table is compiled from tables 1,3,5 of Part II of this series. c noted here is the volume of the sols, viz., 4 ml. of sol A, 4 ml of sol A/1·5 (= 2·66 ml. of A), 4 ml of sol A/2 (= 2·0 ml of A), corresponds to $1/c$ as 0·250, 0·375 and 0·500 respectively.

TABLE 9

(N/40 K$_2$SO$_4$ ml) (ml)	Values of $1/c^2t$ for		
	$1/c = 0.250$	$1/c = 0.375$	$1/c = 0.500$
Sol B :			
0·80	0·00168	0·00379	0·02080
Sol C :			
0·70	0·00137	0·00136	0·03125
0·65	0·00735	0·00740	0·01920

This table is compiled from tables 4 and 6 of Part II of this series.

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The results presented in the above tables are plotted in figs. 3 and 4. It is seen that the plots of $1/c$ and $1/c^2t$ are straight lines, establishing the validity of equation (1).

FIG 3. $\frac{1}{c^2t}$ versus $\frac{1}{c}$

FIG. 4. $\frac{1}{c^2t}$ versus $\frac{1}{c}$
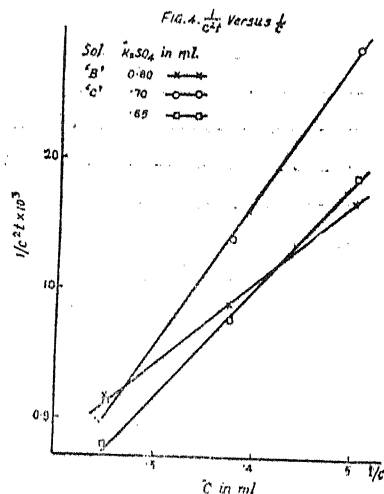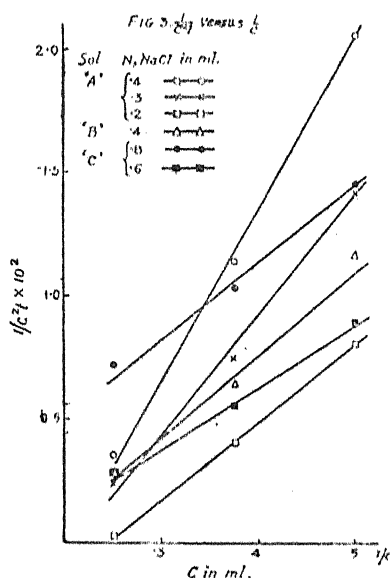
DISCUSSION

The formation of succinate gels by the interaction of sodium succinate and the chloride of either iron or aluminium may be pictured as follows : As sodium succinate is gradually added, say, to a ferric chloride solution, the precipitate of ferric succinate which first appears in colloidal state is peptised by excess of the metal chloride present. The colloidal particles are charged with positive electricity due to the preferrential adsorption of the metal cations and also of the hydronium ions obtained by the hydrolysis of the metal salt. The charges on the particles will gradually decrease due to the removal of the free metal cations by the progressive addition of the sodium succinate. In this manner the unstability of the colloidal particles is suitably controlled and gels are obtained.

If we consider the colloidal particles to be equally hydrated for the different concentrations of the insoluble succinates and also carry the same amount of electric charge due to the presence of the same amount of electrolyte in the sol, gelation occurs as soon as the colloidal particles are attracted and fall in the pocket of least potential to provide the gel a structure. In these circumstances, gelation will occur when a definite number of colloidal particles assume a structure necessary to induce in the system sufficient rigidity. This view when applied to the Smoluchowski's equation for coagulation gives us the relation (1) deduced by Ghosh (*loc. cit*), the validity of which has been established in this paper for the gelation of iron and aluminium succinates.

In view of the above it is evident that gelation is something like coagulation, and it appears, that in the gelation process the aggregation forces of the colloidal units are weak leading to the development of a loose structure embodying large quantities of the solvent, the structural elements being so labile as to be easily destroyed by shaking and repairing themselves when left undisturbed.

[123]

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THE INFLUENCE OF THE CONCENTRATION OF THE GELATING

MATERIAL ON THE GELLING TIME OF SOME SUCCINATE GELS: PART II

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ABSTRACT

Gelation of ferric succinate sols at different concentrations and purity by univalent and bivalent electrolytes has been investigated. The results obtained have been discussed from the point of view of Burton's rule for the coagulation of sols. It is observed that the rule is applicable to impure samples of the sol. For pure sols, however, the ordinary relation, *viz.*, the greater the concentration of the sol the greater is the gelling time, is valid. It is further observed that divergence from the rule is also noticed for highly diluted sols with bivalent sulphate gelating ions. It is emphasised that coagulation and gelation are similar processes.

The coagulation of various sols by electrolytes is of great interest in colloidal studies. Some such sols are recognised for their dual role and possess both lyophobic and lyophilic characteristics. They can be easily coagulated and under suitable conditions yield gels. In coagulation, however, the precipitation values for different concentrations of the sols have been investigated by several workers. Thus, Burton and Bishop (1) formulated a rule which states that with the decrease in the concentration of the colloid the flocculation value increases with univalent ions, remains the same with bivalent ions and varies directly with the concentration of the colloid with trivalent ions. Mukherjee (2), Oden (3), Ghosh and Dhar (4) observed that the flocculation values depend upon the degree of dilution of the sols. Tuller and Fulmer (5) working with emulsions of aniline in water showed that concentrated emulsions are less stable towards all kinds of electrolytes than are dilute emulsions. Exceptions to the Burton's rule are thus known.

In this paper we are recording our observations on the gelation of ferric succinate sols. The gels have been prepared by the coagulation of ferric succinate sols by univalent and bivalent electrolytes. The influence of the concentrations of the sols on the gelling time has been investigated and the results have been discussed from the point of view of the applicability of the Burton's rule.

EXPERIMENTAL

The positively charged sol of ferric succinate is prepared by the method described by Bose and Mushran (6). Ferric succinate is first precipitated by the addition of an excess of sodium succinate solution to a ferric chloride solution. The fresh precipitate is thoroughly washed in a Buchner funnel till the washwater is free from chloride and succinate ions as tested with silver nitrate. The washing is completed within a day to avoid the ageing of the precipitate. The precipitate is shaken with different quantities of succinic acid and the peptisation is complete within a few hours. Transparent wine red sols of ferric succinate are thereby obtained. The sols are easily coagulated with electrolytes and under suitable conditions give transparent and stable gels.

Four samples of the ferric succinate sols are prepared using different amounts of succinic acid. The iron content in each sample is kept the same. Each sample had the following composition :

Total volume = 750 ml.

Total Fe^{+++} content = 0.01972 gm.

Sol	M/2 Succinic Acid
A	100.0 ml.
B	150.0 ml.
C	200.0 ml.
D	250.0 ml.

These are then diluted 1.5 and 2 times and thus the sols, A, A/1.5 and A/2 are obtained. They are preserved at a low temperature, in order to avoid the ageing of the sols, which greatly affects their stability. The gelling times are determined accurately by the 'gel indicator' at 32±0.1°C. The electrolytes used for gelation were sodium chloride and potassium sulphate solutions of suitable concentration. The results obtained are presented in tables 1 to 8.

TABLE 1

Gelling time for :

Sol (A, A/1.5, A/2) = 4.0 ml.

Total Volume = 5.0 ml.

N NaCl	A	A/1.5	A/2
0.4	20.0	13.0	12.5
0.3	30.0	21.0	18.0
0.2	70.0	40.0	33.0
0.1	loose gel	65.0	52.0
(ml)	(mins)	(mins)	(mins)

TABLE 2

Gelling time for :

Sol (A, A/1.5, A/2) = 4.0 ml.

Total Volume = 5.0 ml.

N/40 K$_2$SO$_4$	A	A/1.5	A/2
0.80	Loose gel	10.0	Immediate
0.75	"	14.0	8.0
0.70	"	23.0	10.0
0.65	"	42.0	14.0
(ml)	(mins)	(mins)	(mins)

TABLE 3
Gelling time for :
Sol (B, B/1·5, B/2) = 4·0 ml.
Total Volume = 5·0 ml.

N NaCl	B	B/1·5	B/2
0·7	13·0	12·5	11·5
0·6	16·0	15·0	14·5
0·5		19·0	17·5
0·4 (ml)	25·0 (mins)	20·0 (mins)	22·0 (mins)

TABLE 4
Gelling time for :
Sol (B, B/1·5, B/2) = 4·0 ml.
Total Volume = 5·0 ml.

N/40 K_2SO_4	B	B/1·5	B/2
0·85	25·0	12·0	Immediate
0·80	37·0	16·0	14·5
0·75	51·0	25·0	16·0
0·70 (ml)	loose gel (mins)	34·0 (mins)	19·0 (mins)

TABLE 5
Gelling time for :
Sol (C, C/1·5, C/2) = 4·0 ml.
Total Volume = 5·0 ml.

N NaCl	C	C/1·5	C/2
0·9	Immediate	14·0	15·5
0·8	9·0	16·0	18·0
0·7	16·0	20·0	23·0
0·6 (ml)	25·0 (mins)	28·0 (mins)	29·0 (mins)

TABLE 6
Gelling time for :
Sol (C, C/1·5, C/2) = 4·0 ml.
Total Volume = 5·0 ml.

N/40 K$_2$SO$_4$	C	C/1·5	C/2
0·70	45·0	10·5	8·5
0·65	85·0	19·0	13·0
0·60	loose gel	45·0	23·0
0·55 (ml)	,, (mins)	70·0 (mins)	42·0 (mins)

TABLE 7
Gelling time for :
Sol (D, D/1·5, D/2) = 4·0 ml.
Total Volume = 5·0 ml.

NaCl*	D	D/1·5	D/2
1·0	13·0	9·0	13·0
0·9	21·0	13·0	17·0
0·8	31·0	20·0	24·0
0·7 (ml)	47·0 (mins)	30·0 (mins)	36·0 (mins)

TABLE 8
Gelling time for :
Sol (D, D/1·5, D/2)=4·0 ml
Total Volume=5·0 ml

N/40 K$_2$SO$_4$	D	D/1·5	D/2
0·90	60·0	15·0	Immediate
0·85	95·0	21·0	,,
0 80	loose gel	30·0	13·5
0·75 (ml)	,, (mins)	55·0 (mins)	20·0 (mins)

*Sols D/1·5 and D/2 required 1·5 N NaCl for gelation whereas D required N NaCl.

DISCUSSION

From the results presented in the above table it is interesting to note that for the gelation of ferric succinate sols Burton's rule appears to be applicable when the sols contain large amount of succinic acid. When, however, the amount of the stabilising agent present is less, the diluted sol requires lesser quantity of sodium chloride to bring about the gelation in the same time. Ghosh and Dhar (*loc. cit*) investigating the effect of dilution on the precipitation values by different electrolytes for over twenty different sols, arrived at the conclusion that the Burton's rule is applicable to some sols, whilst the ordinary relation that greater the concentration of the sol the greater is the precipitation value is true for several sols as those of hydrous oxides of iron, aluminium and chromium. Wannow and collaborators (8) report that Burton's rule is applicable for these hydrous oxide sols specially for sufficiently dilute ones. Sorum (9) observed that the effect of dilution on the stability of hydrous ferric oxide towards electrolytes is affected by its purity. In the gelation of ferric succinate sols investigated by us the stability is greatly reduced by employing lesser quantities of the peptising agent *i.e.* succinic acid and in such sols *viz.*, A and B, which are relatively purer the monovalent ions show a behaviour similar to bivalent gelating ions (Tables 1 to 4). In less pure sols *viz.* C and D however, *i. e.* sols containing larger amounts of succinic acid it is highly probable that the stability of dilute sols specially towords monovalent gelating ions (Tables 5 and 7) is due to the lesser probability of contact between the charged colloidal particles and the gelating ions.

It is of interest to mention here that the divergence from the Burton's rule is also noticed for bivalent sulphate ions in case of highly diluted ferric succinate sols. Though the exact gelling time could not be recorded to support this fact due to the loose setting of the gel, but the effect of dilution was clearly perceptible by the slow movement of the drop of the 'gel indicator' in the gelating material. This observation of ours is similar to that of Wannow (*loc. cit*). Our results therefore on the gelation of ferric succinate sols are similar to the observations found in literature on coagulation of several sols and provides verification of the fact that coagulation and gelation are similar processsess.

ACKNOWLEDGMENT

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STUDY OF COLOUR AND CONSTITUTION OF THE DYES OBTAINED FROM SUCCINIC ACID AND SUBSTITUTED SUCCINIC ACIDS

Part II.   Dyes from Phenylsuccinic acid

By

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ABSTRACT

The following dyes have been prepared from phenylsuccinic acid, their properties studied and absorption maxima measured : —

Phenol phenylsuccinein, resorcinol phenylsuccincin, phenyl succinylcosin, phloroglucinol phenyl succinein, quinol phenyl succinein.

In the first paper of this series[1] we had described the preparation and study of succineins. In this second paper the experimental work relating to the preparation and study of phenylsuccineins is given.

Phenylsuccinic acid was prepared by the method described in Organic Synthesis (Vol VII, page 20 and vol. VIII, page 88.)

Phenol phenylsuccinein
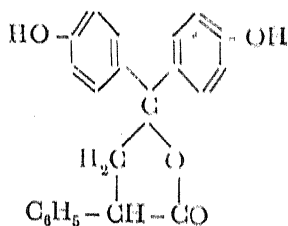
Preparation— A mixture of 2 gms. of the acid and 2 gms. (excess) of phenol was taken and heated in an oil bath with a few drops (8-10) of concentrated sulphuric acid as condensing agent. The heating was continued for 12 hours at a temperature of 115-120°C. The dark viscous condensed mass was then poured into about 100 c.c. of distilled water and subjected to steam distillation to remove excess of phenol. The crude product left behind in the retort was finally powdered and washed well with water under suction. It was then extracted with a very dilute (2%) solution of sodium hydroxide and filtered. From the deep pink alkaline filtrate the dye was precipitated by the gradual addition of dilute acetic acid, and finally with a few drops of dilute hydrochloric acid with constant stirring. The brownish dye was filtered, washed well with water and dried in an oven at 100°C.

For purification, the dye was dissolved in 40 c.c. of absolute alcohol, mixed with half a gram of animal charcoal and refluxed on a steam bath for about an

hour. The mixture was filtered while hot and the residue washed twice with 100 c.c. portions of absolute alcohol. The filtrate and the washings after collecting in a beaker were evaporated to one-third of its volume on a steam bath. The concentrated alcoholic solution after cooling was treated with cold distilled water with constant stirring and the volume raised to about five and a half time. It was filtered again from some sticky substance and the turbid filtrate was again evaporated over a steam bath till the volume was reduced to one-eighth of its original volume. A pinch of A.R. sodium chloride was then added and the whole mixture after stirring well was kept overnight when the dye separated out in the form of a light brown powder. This was filtered, collected and dried in an oven at 100°C.

Properties —The dye is light brown in colour. It dissolves in alcohol giving an yellow solution which turns pink on addition of a drop of alkali. With alkali it gives a light red colour. The freshly prepared dye, however, gives pink colour with alkali. It melts at 142°C and absorbs at 5400 Å.

Analysis:—Found : C=75·8%, H=5·54%, the formula $C_{22}H_{18}O_4$ requires C = 76·30%, H = 5·20%.

Resorcinol Phenylsuccinein (Phenyl Succinylfluorescein
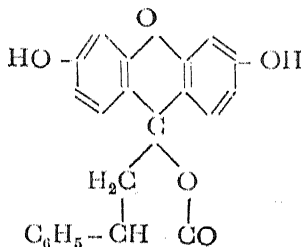
Preparation:—An intimate mixture of 20 gms. of the acid and 34 gms. of resorcinol was heated in a conical flask to a temperature of 140°C in an oil bath. When the mass melted a few drops (10-12) of concentrated sulphuric acid were added and the whole mass stirred well with a glass rod. When the vigorous reaction had subsided the temperature was raised to 160°C and kept there for four hours during which time the contents of the flask had almost become solid. After cooling, the condensed mass was finally powdered, extracted with a dilute 3% solution of sodium hydroxide and filtered. From the deep red alkaline filtrate the dye was precipitated by the gradual addition of dilute hydrochloric acid with constant stirring, avoiding a temporary local excess of the acid which causes the precipitate to ball together. It was filtered, washed well with water and dried in an oven at 110°C.

The brown amorphous dye was boiled with alcohol. A major portion of the dye dissolved, leaving an orange coloured residue. Thus, it appears that the dye consists of two components, one is alcohol soluble and the other is alcohol insoluble.*

---

*The alcohol insoluble portion of the dye has been studied by Arthur Lapworth and John Alexander McRae (*J. Chem. Soc.*, 1922, T, 2723). The dye obtained by them is orange in colour and has a melting point of 249°C.

From the alcoholic solution, the dye was precipitated by the gradual addition of ice cold distilled water with constant stirring. During this process care was taken that the temperature did not rise appreciably as it resulted in the formation of a gummy mass, which had to be dissolved again by the addition of fresh alcohol and the whole process repeated again. It was filtered and dried in an oven. The dye, when crystallised thrice with alcohol, gave a pure brown amorphous powder which was filtered off under suction and dried in an oven at 110°C.

Properties :—It is a dark brown amorphous powder. It dissolves in alcohol giving an yellow solution with a light green fluorescence. With aqueous sodium hydroxide it gives a red solution which on dilution shows intense green fluorescence, comparable with the other fluorescences under similar circumstances. It melts at 200°C. Its neutral solution has absorption maximum at 4600 Å and the alcoholic solution containing a drop of alkali at 4900 Å.

Analysis :—Found: C = 73·6%, H = 4·5%, the formula $C_{29}H_{16}O_5$ requires C = 73·33%, H = 4·4%.

Acetylation of Resorcinol phenylsuccinein :—0·5 gm. of the dye, 15 c.c. (excess) of acetic anhydride add 2·50 gms. of freshly fused sodium acetate were taken in a 50 c.c. round bottom flask fitted with an air condenser and the contents refluxed over a sand bath for four and a half hours. The contents of the flask were then poured into a beaker, three fourths filled with water, and stirred well. A brown precipitate settled down which was filtered off under suction, washed well with water and dried. The crude acetylated product when purified by crystallisation from acetone gave a semi-crystalline brown compound.

Analysis of Acetylated Resorcinol phenylsuccinein :—Found: C = 70·17%, H = 4·45%, the formula $C_{26}H_{20}O_7$ requires C = 70·28%, H = 4·50%

On hydrolysing the acetylated product the percentage of the acetyl groups present in the acetyl derivative was found to be 19·3%, which corresponds to two hydroxyl groups in the parent dye molecule.

Caustic potash fusion of Resorcinol phenylsuccinein :—15·0 gms. (excess) of caustic potash were heated to a temperature of 275°C with a few drops of water over a sand bath in a nickel crucible and to this were added 5·0 gms. of the dye in 0·25 gm. portion at a time. The frothing mixture was stirred well with a glass rod after each addition. The heating was continued at 275-280°C for about three and a half hours. After cooling, the mass was dissolved in large excess of distilled water and filtered. The alkaline filtrate was then acidified with dilute hydrochloric acid when a slightly brown compound was obtained. This compound when crystallised from alcohol gave an almost colourless compound having acidic properties. The compound could not be identified owing to the paucity of the yield.

This acidic compound was then condensed with resorcinol in the presence of sulphuric acid as condensing agent at a temperature of 160°C. The dye thus obtained after purification was found to be indentical with the original dye.

Fusion with potash was also tried under different conditions i.e. by refluxing the dye with 25%, 50% and 100% of caustic potash solution over an oil bath, a sand bath and even over a naked flame, but no satisfactory result was obtained.

[132]

Bromination of Resorcinol phenylsuccinein: 2:4:7:9—*Tetrabromo-resorcinol phenylsuccinein* (Phenyl succinyleosin): ·

$$
\begin{array}{c}
\text{HO} - \overset{\text{Br}}{\underset{}{\diagup\diagdown}} \diagup \overset{\text{O}}{\diagdown} \overset{\text{Br}}{\underset{}{\diagup\diagdown}} - \text{OH} \\
\text{Br} - \diagdown\diagup \diagdown \underset{\text{C}}{\diagup} \diagdown\diagup - \text{Br} \\
\text{H}_2\text{C} \quad \text{O} \\
\text{C}_6\text{H}_5 - \text{CH} - \text{CO}
\end{array}
$$
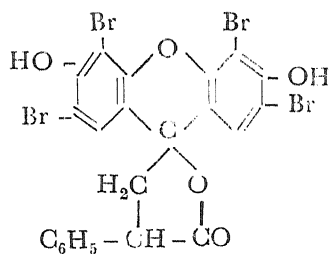
2 gms. of resorcinol phenylsuccinein were dissolved in 20 c.c. of alcohol in a 150. c.c. conical flask. The flask with its contents was cooled in an ice bath and 2 c.c. (excess) of bromine were then added from a dropping funnel drop by drop, shaking the flask after each addition. When all the bromine had been added, the mixture was shaken well and kept overnight to ensure complete bromination. It was then poured into about 300 c.c. of cold distilled water and stirred well. The red coloured brown derivative thus separated was filtered under suction and washed well with water in order to remove excess of bromine. The washed product was then dissolved in dilute caustic soda solution and filtered. The red alkaline filtrate was acidified by the gradual addition of dilute hydrochloric acid with constant stirring, which caused the precipitation of the bromo derivative as a red substance. The precipitated bromo derivative was filtered and washed well with water again. Finally, it was purified by crystallisation from alcohol. It was filtered under suction and dried in an oven at 110·C.

The bromo derivative of resorcinol phenylsuccinein is brick red in colour. It dissolves in alkali giving a dark red solution. Its solution in alcohol is also red but the intensity is not of the same order as in the case of alkaline solution. It softens at 162° and melts at 167-168°. Its absorption maximum lies at 5100 Å.

Analysis gave the following results: Br=47·12%, the formula $C_{22}H_{12}O_6Br_4$ requires Br=47·34%.

The percentage of bromine shows that it is a tetrabromo derivative of resorcinol phenylsuccinein.

[A tetrabromo derivative from alcohol insoluble component of resorcinol phenylsuccinein has been reported by Arthur Lapworth and John Alexander McRae[2]. The tetrabromo derivative obtained by them was almost colourless and became somewhat pink on keeping in a desiccator. It melted at 295°C.]

The other dyes from phenylsuccinic acid were prepared in the same manner as resorcinol phenylsuccinein. The experimental conditions for the preparation of

these dyes are given below in a tabular form. The condensation in all these cases was done in the presence of two drops of concentrated sulphuric acid.

Name of the Dye	Temperature	Duration of heating	Melting point	Absorption max
Phloroglucinol phenylsuccinein	180-200°	2 hrs.	above 300°	4600 λ
Pyrogallol phenylsuccinein	160-180°	4 hrs.	,,	4400 λ
Catechol phenylsuccinein	170-175°	4½ hrs.	,,	4600 λ
Quinol phenyl-succinein	160-180°	5 hrs.	,,	4600 λ

Phloroglucinol phenylsuccinein :— HO —[structure] OH
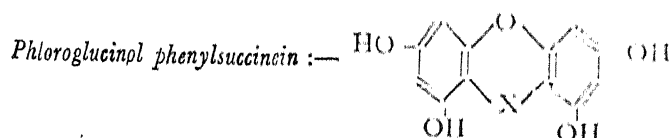
In the above formula and in the formulae occurring latter in this paper X represents

$$\begin{array}{c} >C< \\ H_2C \quad O \\ | \quad\quad | \\ C_6H_5 - CH --- CO \end{array}$$
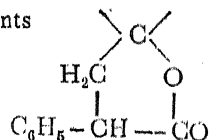
It is a brown solid. It dissolves in alcohol giving a reddish yellow solution which turns red on the addition of a drop of alkali. With dilute alkali solution it gives deep red colour.

Analysis gave the following results :—

C $= 65\cdot50\%$, H $= 4\cdot22\%$, the formula $C_{22}H_{16}O_7$ requires C $= 65\cdot82\%$, H $= 4\cdot08\%$.

Pyrogallol Phenylsuccinein :— HO —[structure] OH
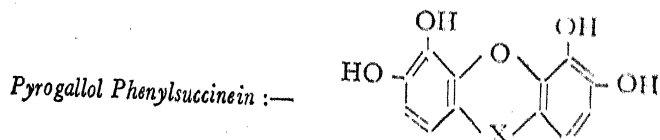
It is a dark brown solid. Its solution in alcohol is light brown and in alkali the solution is dark brown which darkens further on keeping.

[134]

Analysis gave the following results :—

$C = 65 \cdot 62\%$, $H = 4 \cdot 31\%$, the formula $C_{22}H_{16}O_7$ requires $C = 65 \cdot 82\%$, $H = 4 \cdot 08\%$.

Catechol Phenylsuccinein :—
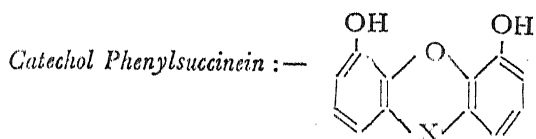
It is a black solid soluble in alcohol giving a reddish brown solution. Its solution in alkali is brown.

Analysis gave the following results :—

$C = 74 \cdot 02\%$, $H = 4 \cdot 62\%$, the formula $C_{22}H_{16}O_5$ requires $C = 73 \cdot 33\%$, $H = 4 \cdot 44\%$.

Quinol Phenylsuccinein :—
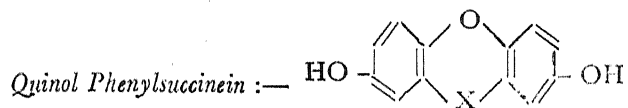
It is a black coloured solid and dissolves in alcohol giving a brown solution. Its solution in dilute caustic alkali is dark brown.

Analysis gave the following results :—

$C = 73 \cdot 72\%$, $H = 4 \cdot 46\%$, the formula $C_{22}H_{16}O_5$ requires $C = 73 \cdot 33\%$, $H = 4 \cdot 44\%$.

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STUDIES ON THIOARSENATES

PART I: PRECIPITATION OF ARSENIC PENTASULPHIDE

By

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ABSTRACT

The precipitation of arsenic pentasulphide by decomposing its thiosalt with acid has been studied. It has been found that complete precipitation occurs when As : NaHS 1 : 4, and the whole of arsenic is converted to thioarsenate. The acidity of the medium also plays a vital role, because precipitation occurs by the slow decomposition of molecular thioarsenic acid whose dissociation is first to be checked by adding acid. The pH of the solution also rises slowly as the decomposition proceeds precipitating As_2S_5.

A similar rise of pH with time is also witnessed in the case of NaH_2AsS_4 and Na_2HAsS_4 solutions. It is probably due to the hydrolysis of these salts, which results in the liberation of some free alkali.

In an earlier communication[1] from this laboratory the results on the study of thioarsenite have been reported. It was concluded that with the progressive addition of hydrosulphide reagent to an arsenite solution, thioxyarsenites with increasing number of sulphur atoms are formed stepwise, finally giving the thioarsenite. On adding acid to these salts, the corresponding thioacids are formed. With increasing acidity of the medium the decomposition of thioarsenious acid is checked to give undissociated thioacid molecules, which decompose to give a precipitate of As_2S_3, liberating H_2S. The present paper deals with the study of thioarsenates.

It has been found that the precipitations of arsenic pentasulphide by decomposing the thiosalt with HCl is complete only when four mols of sulphur as NaHS to each of arsenic atom have been added. With only one equivalents of NaHS, only sulphur is precipitated and the amounts of sulphur thus separated, decrease, with the increase in the amounts of added NaHS, so that finally the precipitate obtained by the decomposition of thioarsenate is practically free of any sulphur.[2] Thus with the progressive addition of NaHS solution thioxyarsenates *viz.* Na_3AsSO_3, $Na_3AsS_2O_2$, and Na_3AsS_3O are formed stepwise, finally giving the thioarsenate Na_3AsS_4. On adding acids, the corresponding thioxy and thioacids are formed. With increasing acidity undissociated thioarsenic acid molecules are formed which really decompose to give a precipitate of As_2S_5 liberating H_2S. This decomposition of the thioarsenic acid molecules is, however, very slow. It can be enhanced by heating the reaction mixture to boiling. Here some H_2S escapes, so that the amounts precipitated even from 4 moles of NaHS are slightly less than the theoretical value. One more interesting feature of this precipitation is that along with the decomposition the pH of the solution also rises slowly. It can be attributed to the gradual replacement of the thioarsenic acid with a weaker acid H_2S.

EXPERIMENTAL

A 0·5 M solution of sodium arsenate $Na_2HAsO_4 . 7H_2O$ (Merck quality) was prepared, and standardized by precipitating arsenic as As_2S_5. The reagent NaHS was prepared as outlined before.[1]
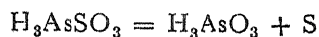
Precipitations by varying amounts of NaHS :—

A standard 0·05 M sodium arsenate solution (10 c.c.) was treated with varying amounts of a 0·1 M NaHS solution and acidified with an equal volumes of conc. hydrochloric acid, so that its final concentration is approximately 6 N in the mixture. In one set of experiments the mixtures were heated to boiling to decompose the thiosalt, whereas the others were left overnight. The precipitates so obtained were filtered through weighed sintered glass crucibles (G—4) washed throughly with water, alcohol and carbon disulphide to dissolve out any free sulphur, dried at 100.-110°C and weighed. The results are given in table 1.

TABLE 1

(Standard value=0·0774 g.)

0·05 M arsenate soln. (c.c.)	0·1 M NaHS (c.c.)	Conc. HCl (c.c.)	As_2S_5 precipitate in g.	
			By slow decomposition	By boiling
10	5	15	0·0012	0·0000
10	10	20	0·0338	0·0320
10	15	25	0·0636	0·0632
10	20	30	0·0772	0·0746
10	25	35	0·0770	0·0772
10	30	40	0·0776	...

It is seen that complete precipitation occurs by slow decomposition, when As:NaHS=1·4 in the system. When boiled the results are slightly less, because some H_2S escapes. With only one mol. of NaHS practically no precipitate of arsenic pentasulphide is obtained. Only sulphur separates, which was filtered off, and the filtrate was tested for arsenite iodimetrically with positive results. It indicates the reaction to occur as

$$H_3AsSO_3 = H_3AsO_3 + S$$

Precipitation by varying amounts of HCl :

To test the effect of the acid concentration on the precipitation of As_2S_5, the solutions containing the thiosalt (formed by mixing 10 c.c. 0·05 M sodium arsenate + 20 c.c. of 0·1 M NaHS) were acidified with varying amounts of 0·1 M HCl and left overnight, 2 c.c. of $BaCl_2$ solution was added in each case to coagulate the precipitates completely. The precipitates thus obtained were filtered through weighed sintered glass crucibles, washed thoroughly with water, dried at 100-110°C and weighed. The precipitates were again washed thoroughly with alcohol and carbon-disulphide to dissolve out free sulphur and reweighed. The weights of sulphur admixed with the precipitates were obtained by difference. The final pH value of these mixture solutions was also noted. The results are given in table 2.

[137]

TABLE 2

Standard 0·0774 g.

0·1 M HCl (c.c.)	Wt. of sulphide (g)	Wt. of sulphur (g)	pH
20	0·0000	0·0070	6·90
25	0·0112	0·0016	5·80
26	0·0256	0·0012	5·78
27	0·0392	0·0016	5·76
28	0·0516	0·0014	5·64
29	0·0632	0·0012	5·40
30	0·0780	0·0014	3·20
35	0·0780	0·0012	2·36
40	0·0778	0·0012	2·20

From the proportions of the acid added in the mixture the various acid salts formed can be calculated and it will be seen that from the compound Na_2HAsS_4, only sulphur separates. The precipitation of arsenic pentasulphide begins when all but one sodium have been neutralised to give NaH_2AsS_4, and is completed when all the thiosalt has been converted into the thio-acid H_3AsS_4 (i.e. at 6 equivalents of HCl). It will be seen that on adding 25 c.c. or more of the acid, the amount of the sulphur separated becomes considerably small. It appears that in the first case some thioxy arsenate is also present, which liberates sulphur. It is natural, because with increasing acidity of the medium the formation of thio-arsenate is enhanced (Part II of this paper), and with the increase in alkali the process is reversed. It is expected, therefore, that a solution corresponding to Na_2HAsS_4 being at higher pH may have more of the thioxy compounds, thus liberting more sulphur.
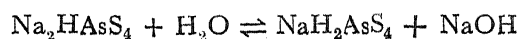
Slow decomposition of thioarsenate with HCl (Rise in pH with time) :—

25 c.c. of 0·05 M sodium arsenate was mixed with 50 c.c. of 0·1 M NaHS to form the thio arsenate (Na_3AsS_4) completely and then acidified with varying amounts (75, 62·5, 50 c.c.) of 0·1 M HCl corresponding to form H_3AsS_4 NaH_2AsS_4, and Na_2HAsS_4 respectively. The total volume was raised to 200 c.c. in each case. The pH of these solutions was measured with time. The results are given below in Table 3.

TABLE 3

Time (Minute)	pH		
	H_3AsS_4	NaH_2AsS_4	Na_2HAsS_4
0	2·38	3·70	6·50
5	2·64	3·78	6·50
10	2·70	3·88	...
15	2·72	3·98	6·52
20	2·76	4·10	...
30	2·78	4·34	6·56
45	2·78	4·68	6·58
60	2·80	4·90	6·58
75	...	5·06	...
90	...	5·18	...
120	...	5·30	...
∞	3·34	6·12	6·78

It will be seen that the change in pH with time is most marked in the case of NaH_2AsS_4. In the case of H_3AsS_4, the rise can be attributed to the replacement of stronger thioarsenic acid by a weaker acid H_2S. From a solution of NaH_2AsS_4 some precipitate of arsenic sulphide is also obtained. Thus the rise of pH may be ascribed to the hydrolysis of these salts liberating free alkali and forming some thioacid H_3AsS_4, which decomposes slowly to give a precipitate of arsenic sulphide, as shown below : —

$$Na_2HAsS_4 + H_2O \rightleftharpoons NaH_2AsS_4 + NaOH$$

$$NaH_2AsS_4 + H_2O \rightleftharpoons H_3AsS_4 + NaOH$$

$$2\,H_3AsS_4 \xrightarrow{slow} As_2S_5 + 3\,H_2S.$$
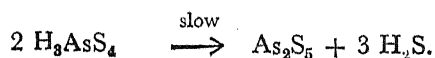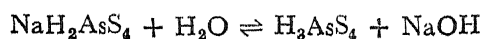
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AMINO ACID MAKE-UP OF PROTEINS IN DOLICHOS BIFLORUS AND GLYCINE SAJA

By

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ABSTRACT

Water, 10% NaCl, 0·2% NaOH and 80% alcohol have been used to isolate proteins from Dolichos biflorus and Glycine saja. Arginine, Ornithine, Histidine, Aspartic acid, Serine, Glutamic acid, Alanine Tyrosine, Methionine, Valine, Phenylalanine and Leucine have been found to be present in both these cereals. Glycine saja, however, contains Glycine in addition.

Kumaon region is very rich in wild vegetation but on account of inadequate irrigation facilities and limited cultivable land the yield of cereals and other cultivated products is very poor. Amongst the cereals grown in this region, mention may be made of Dolichos biflorus (local name Gahat) and Glycine saja (local name — Bhatt) which belong to the leguminosae family. The local people believe that these cereals are very useful from nutritional point of view. They are, therefore, widely used and form special dishes of every home here in place of cereals cultivated in the plains. It was, therefore, considered worthwhile to isolate their protein matter and to study their amino acid make-up in order to from an idea about their nutritive value. In this article, the authors describe the isolation of proteins and the characterisation of amino acids in the protein hydrolysates by descending paper chromatographic technique.

EXPERIMENTAL

The most common methods, generally employed to isolate proteins from plants and seeds, make use of water, neutral saline solution, 70-80% alcohol, and very dilute solutions of acids and alkalis.[1] No single solvent was found suitable to isolate completely the protein matter from Dolichos biflorus and Glycine saja.

(a) *Isolation of protein matter from Dolichos biflorus and Glycine saja :—*

75 gms of the finely powdered material was treated successively with water, 10% NaCl solution, 0·2% NaOH solution and 80% alcohol.

75 gms of the fine powder was mixed with 750 c.c. of distilled water and stirred by means of an electrical stirrer for about three hours and then filtered. The residue

(No. 1) was shaken with 375 c.c. of 10% NaCl solution, stirred for two hours and filtered. This second residue (No. 2) was freed from NaCl by washing with distilled water a number of times and then stirred with 0·2% NaOH solution for two hours and finally filtered. The residue (No. 3) was freed from NaOH by washing with distilled water, stirred with 375 c.c. of 80% alcohol for two hours and filtered. The final reside (No. 4) obtained after extracting the cereal material with water, 10% NaCl solution, 0·2% NaOH solution, and 80% alcohol did not give a positive test for nitrogen. Thus the protein matter of both the cereals is completely extracted by the above solvents.

The water, 10% NaCl, 0·2% NaOH and 80% alcohol soluble protein matter was dialysed separately for 4-5 days and the dialysate evaporated over water bath.

(b) Hydrolysis of the protein matter :—

0·2-0·5 gms of the protein material from each extract was separately refluxed with 20 c.c. of 6N HCl for 12 hours on a sand bath. The hydrolysate was, then, taken in a porcelain dish and most of the acid was removed by evaporation over a water bath. Evaporation was continued, repeatedly adding distilled water, till the vapours did not give white fumes with ammonia. The last traces of acid were removed by keeping the hydrolysate inside a vacuum desiccator containing a small amount of solid KOH. Each of the hydrolysates was then extracted with absolute alcohol.

(c) Characterisation of amino acids in protein hydrolysates :—

Amino acids were characterised by employing descending paper chromatographic technique. 0·004 ml – 0·008 ml of protein hydrolysates and 0·002 ml of 0·1% solutions of reference amino acids were chromatographed together on Whatman filter paper No. 1 (sheets 48 × 28 cms). The paper was equilibrated with the lower layer of butanol— acetic acid—water[2] (4:1:5, v/v) for 24 hours. The chromatogram was developed by the upper layer (solvent phase) of the above mixture for 36 hours at $18 - 20°C$. The chromatogram was taken out of the chamber, and the boundary of the solvent front was marked. After drying it in the air over-night, it was developed again by the solvent phase till the solvent front reached the marked boundry line. Thus the multi-development process was repeated 3 times in order to achieve better and distinct separation of amino acids. After developing and drying, the chromatogram was sprayed with 0·1% solution of ninhydrin in acetone. Finally it was kept in an electric oven at 55°C for 15 minutes, and the amino acids were located as pink spots.

The R_f values of amino acids used as reference ones are recorded in table No. 1. The total number of amino acids present in the four protein fractions were also confirmed by analysing chromatographically a mixture of the four hydrolysates.

The amino acids present in the protein fractions isolated from Dolichos biflorus and Glycine saja have been recorded in table No. 2 and No. 3 respectively, while table No. 4 gives the amino acids present in the mixture of the hydrolysates obtained from the protein fractions extracted by different solvents.

[141]

TABLE 1

Amino acid		R$_f$ value
Cystine	...	0·05
Arginine	...	0·066
Lysine	...	0·07
Ornithine	...	0·08
Histidine	...	0·107
Aspartic	...	0·11
Serine	...	0·13
Glycine	...	0·16
Glutamic	...	0·18
Alanine	...	0·24
Tyrosine	...	0·35
Methionine	...	0·39
Valine	...	0·45
Tryptophan	...	0·47
Phenylalanine	...	0·57
Isoleucine	...	0·62
Leucine	...	0·66

TABLE 2

Amino acids present in the protein hydrolysates of Dolichos biflorus

S. No.	Protein fraction	Amino acids identified
1	Soluble in water ...	Aspartic, Glutamic, Alanine, Tyrosine Valine, Phenylalanine and Leucine.
2	Soluble in 10% NaCl solution.	Ornithine, Histidine, Serine, Glutamic, Alanine, Tyrosine, Valine and Leucine.
3	Soluble in 0·2% NaOH solution.	Arginine, Histidine, Serine, Glutamic, Alanine, Methionine, Valine, Phenylalanine and Leucine.
4	Soluble in 80% alcohol ...	Aspartic, Serine, Glutamic Alanine, Tyrosine, Valine and Leucine.

TABLE 3

Amino acids present in the protein hydrolysates of Glycine saja

S. No.	Protein fraction		Amino acids identified.
1	Soluble in water	...	Ornithine, Histidine, Glycine, Alanine, Methionine, Valine and Leucine.
2	Soluble in 10% NaCl	...	Ornithine, Aspartic, Serine, Glutamic, Alanine, Tyrosine, Valine and Leucine.
3	Soluble in 0·2% NaOH Solution.		Arginine, Serine, Glutamic, Alanine, Methionine, Valine, Phenylalanine and Leucine.
4	Soluble in 80% alcohol	...	Arginine, Aspartic, Serine, Glutamic, Alanine, Tyrosine, Valine, and Leucine.

TABLE 4

Amino acids present in the mixture of the hydrolysates of Dolichos biflorus and Glycine saja.

S. No.	Cereal		Amino acids identified
1	Dolichos biflorus	...	Arginine, Ornithine, Histidine, Aspartic acid, Serine, Glutamic acid, Alanine, Tyrosine, Methionine, Valine, Phenylalanine and Leucine.
2	Glycine saja	...	Arginine, Ornithine, Histidine, Aspartic acid, Serine, Glycine, Glutamic acid, Alanine, Tyrosine, Methionine, Valine, Phenylalanine and Leucine.

It is interesting to note that Dolichos biflorus and Glycine saja both contain the same essential and non-essential amino acids; Glycine saja, however, contains Glycine in addition. Both these cereals are a source of six essential amino acids in common, thereby, giving some idea about their nutritive value in diet.

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[143]

ADSORPTION OF PHOSPHATE ION BY INDIAN LIME (JABALPUR) AT DIFFERENT pH VALUES, PART I

By

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[Received on 10th August, 1960]

ABSTRACT

A sample of lime from Jabalpur (India) was found to adsorb phosphates from different phosphate solutions at pH (of HCl/NaOH) 4 to 10. Little fixation was recorded from phosphoric acid at pH 4. In the acidic range and from the acid phosphate solutions added; the fixation is contemplated to have taken place as a result of surface reaction. From basic phosphates the fixation is, however, supposed to be more due to the formation of dicalcium and tricalcium phosphates than simple adsorption. In the alkaline range the fixation noted from all the phosphates is also explained as a result of the formation of dicalcium and tricalcium phosphates. In all the cases, fixation increased with the increase of pH and alkalinity of the added phosphate solution.

Considerable interest was stimulated in the problem of the relation of phosphate fixation with pH by Roszmann's paper[1] in 1927 in which the influence of pH on phosphate retention was accurately shown. The interest was further enhanced with the publication of a paper by Bradfield, Scarseth and Steele[2] in which three separate mechanisms of phosphate fixation overlapping in nature were postulated. In a recent paper, Mattson[3] has also reached a similar conclusion and shown the relation between phosphate fixation and pH from his curves which registered four maxima. However, it is important to note that the form of phosphates that are obtained either from surface reaction or chemical precipitation have all been claimed to be complex in nature and of uncertain composition. Thus, under soil conditions Cameron and Bell[4] suggested the existence of a series of solid solutions of phosphoric acid and lime. In 1927, Bassett[5] claimed hydroxy apatite as the sole durable compound that can exist in soil. Further, McGeorge and Breazeale[6] suggested that in calcium-rich soils the insoluble phosphate is carbonate-phosphate compound which is formed from the combination of one mole of calcium carbonate and three moles of tricalcium phosphate. Many others, including McIntire and Hatcher[7] believed in the possible reversion of super-phosphate to a fluor-phosphate when incorporated into limed soils. It is evident, therefore, that the fixation of phosphate is mainly a function of pH and the compounds that are formed are complex and of variable nature.

A study of the adsorption of phosphate by lime is deemed necessary because of its accepted role in the above phenomenon in soils and clay minerals containing the material in detectable quantities.

EXPERIMENTAL

Jabalpur limestone was finely powdered and sieved through a 100 mesh sieve. The sieved powder was heated strongly in a platinum crucible over a blow pipe burner for nearly ten hours when a constant weight was attained and carbonate was detected to be absent. This sample of lime was stored in a desiccator over lime for further study. Freshly ignited samples were used for the investigations. 2·5 grams of the lime were taken in different 250 ml. conical flasks and 90 ml. of aqueous solutions of hydrochloric acid or of sodium hydroxide (of known pH

values) were added and were allowed to stand at 30°C for 24 hours. Then to these, 10 ml. of the phosphate solutions containing 30·8046 miligrams P_2O_5 were added. The flasks were allowed to stand in a thermostat at 30°C for another 24 hours and were occasionally shaken. After the period, 10 ml. of the supernatant liquid were pipetted out and P_2O_5 content was estimated by ammonium phosphomolybdate method. The amounts adsorbed (in the following tables) are those by 2·5 grams of the lime.

TABLE 1

Adsorption of phosphate ion from H_3PO_4 (pH 3·8) by lime at 30°C

pH of NCl/NaOH added	Adsorption (mgm.)	pH (lime+HCl/NaOH)	pH of the mixture
(1)	(2)	(3)	(4)
4	0·0000	6·9	3·90
5	0·0618	7·2	3·95
6	0·1236	8·2	4·00
7	0·1854	8·4	2·20
8	0·2472	9·30	4·40
9	0·3399	10·7	4·60
10	0·6798	11·8	4·80

TABLE 2

Adsorption of phosphate ion from $NH_4H_2PO_4$ (pH 4·2) by lime at 30°C

(1)	(2)	(3)	(4)
4	0·0618	6·9	5·10
5	0·0927	7·2	5·90
6	0·1545	8·2	6·60
7	0·2472	8·4	7·90
8	0·4635	9·3	9·20
9	0·6798	10·7	9·50
10	1·2360	11·8	10·40

TABLE 3

Adsorption of phosphate ion from NaH_2PO_4 (pH 5·6) by lime at 30°C

pH of HCl/NaOH added	Adsorption (mgm.)	pH (lime + HCl/NaOH)	pH of the mixture
(1)	(2)	(3)	(4)
4	0·1236	6·9	5·70
5	0·2163	7·2	6·00
6	0·2781	8·2	6·90
7	0·5253	8·4	7·50
8	0·8034	9·3	8·90
9	1·2669	10·7	9·30
10	2·7501	11·8	10·20

TABLE 4

Adsorption of phosphate ion from NH_4NaHPO_4 (pH 8·0) by lime at 30°C

(1)	(2)	(3)	(4)
4	0·2781	6·9	7·10
5	0·4635	7·2	7·30
6	0·5871	8·2	8·00
7	0·9579	8·4	8·10
8	1·4832	9·3	8·60
9	2·7509	10·7	9·80
10	5·3766	11·8	10·30

TABLE 5

Adsorption of phosphate ion from Na_2HPO_4 (pH 8·2) by lime at 30°C

(1)	(2)	(3)	(4)
4	0·8343	6·9	7·20
5	1·3905	7·2	7·40
6	1·7613	8·2	8·20
7	1·9158	8·4	8·30
8	2·9664	9·3	8·90
9	5·1912	10·7	9·95
10	10·4751	11·8	10·50

[146]

TABLE 6

Adsorption of phosphate ion from $(NH_4)_3PO_4$ (pH 8·4) by lime at 30°C

pH of HCl/NaOH added	Adsorption (mgm.)	pH (lime+HCl/NaOH	pH of the mixture
(1)	(2)	(3)	(4)
4	2·5338	6·9	7·40
5	4·2024	7·2	7·70
6	5·5929	8·2	8·30
7	6·0564	8·4	8·40
8	8·8992	9·3	9·30
9	10·3824	10·7	10·30
10	10·2704	11·8	11·80

TABLE 7

Adsorption of phosphate ion from Na_3PO_4 (pH 8·6) by lime at 30°C

(1)	(2)	(3)	(4)
4	5·1912	6·9	7·50
5	7·9413	7·2	7·80
6	10·8768	8·2	8·40
7	12·1437	8·4	8·50
8	17·4276	9·3	9·20
9	20·7339	10·7	10·40
10	24·5037	11·8	10·95

TABLE 8

Adsorption of phosphate ion from K_3PO_4 (pH 9·1) by lime at 30°C

(1)	(2)	(3)	(4)
4	9·3627	6·9	7·60
5	15·3573	7·2	7·90
6	20·1468	8·2	8·50
7	23·2368	8·4	8·60
8	26·9448	9·3	9·20
9	27·9236	10·7	10·60
10	23·7988	11·8	11·00

The experimental results show that the addition of different acid/alkali solutions to lime resulted in each case an increase in pH of the mixtures due to the alkalinity of lime. When different phosphate solutions were added to these mixtures and equilibrated for 24 hours the resulting solutions recorded a decrease in pH except for the three tribasic phosphates. In potassium and sodium phosphates (tribasic) an increase in pH was noted when the initial pH of the acid or alkali was 4 to 7 and in ammonium phosphate (tribasic) at 4 to 6.

The decrease in pH was found to bring about, practically in all cases, phosphate fixation. It is interesting to note that for individual phosphates this fixation increases with the increase of pH and the fixation is more at all pH levels as the pH of the phosphate solutions added became higher. Thus, a small amount of fixation was recorded from phosphoric acid (pH 3·8) and the fixation gradually increased until the maximum was reached in tribasic potassium phosphate (pH 9·1). The percentage of fixation of phosphoric acid at pH 4 is negligible and at pH 10 is only 2·01, whereas the percentage of fixation from tribasic potassium phosphate at pH 4 is 27·69 and at pH 10 as high as 85·19.

Increase in the hydroxyl ion concentration when the desired pH solutions were added to calcium oxide may be explained in the following way. It is well-known that when calcium oxide is subjected to the reaction of acids the corresponding salts are formed. In the acid side, therefore, the increase in pH may be due to the formation of calcium chloride which is less acidic as is evident from the simple equation $CaO + 2HCl \rightarrow CaCl_2 + H_2O$. This reaction is, however, gradually replaced by the equation $CaO + H_2O \rightarrow Ca(OH)_2$, as it approaches the alkaline side. It is evident, therefore, that the increase in alkalinity in the acid and the alkaline side is due to the formation of two different substances, one being less acid in reaction and the other strongly alkaline. In the solutions, therefore, these are the two substances that remain in admixture, depending upon the pH of the medium before the addition of the desired phosphate solutions were made. Naturally, it is expected that in addition to the surface reaction which may also play some role in phosphate fixation when calcium oxide acts as an adsorbent, chemical precipitation of less insoluble phosphates may also occur when these substances are reacted with the different water soluble phosphates. It is also expected that because of different amount of formation of calcium chloride and calcium hydroxide in the acidic and alkaline medium respectively, the nature and amount of insoluble calcium phosphates that are formed under different pH levels would not be the same. Studying the pH change of solutions before and after the addition of phosphates the following series of reactions might be conjectured to have taken place leading to phosphate fixation.

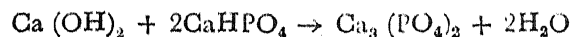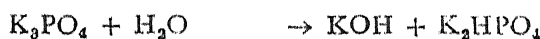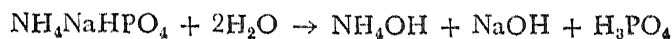**A. Acid Range.** In the acid range the following reactions might have taken place.

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$
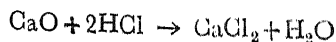
(a) With H_3PO_4, $NH_4H_2PO_4$ and NaH_2PO_4.

$$CaCl_2 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2HCl$$

$$CaCl_2 + 2NH_4H_2PO_4 \rightarrow Ca(H_2PO_4)_2 + 2NH_4Cl$$

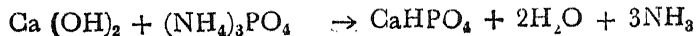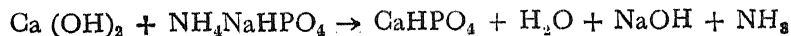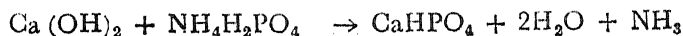$$CaCl_2 + 2NaH_2PO_4 \rightarrow Ca(H_2PO_4)_2 + 2NaCl$$

[148]
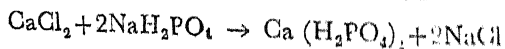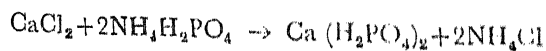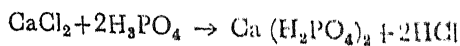
The formation of this monocalcium phosphate seems to have not resulted in the phosphate fixation at low pH when the phosphate added is in the form of H_3PO_4 and $-H_2PO_4$. This is evident from tables 1, 2 and 3 in which the amount of fixation recorded is quite low. It may be noted that the fixation progressively increases at all pH when the pH of the added phosphate solutions become higher. We may, therefore, conclude that at lower pH and from phosphate solutions of higher acidity the fixation of phosphate by calcium oxide is more due to surface reaction than to chemical interaction. It is only at higher pH and from phosphate solutions of higher alkalinity that chemical precipation plays any appreciable role in the fixation of phosphates.

(b) *With* $NH_4,NaHPO_4$ *and* Na_2HPO_4 *and* $(NH_4)_3PO_4$, Na_3PO_4 *and* K_3PO_4.

$$CaCl_2 + NH_4NaHPO_4 \rightarrow CaHPO_4 + NH_4Cl + NaCl$$

$$NH_4NaHPO_4 + 2H_2O \rightarrow NH_4OH + NaOH + H_3PO_4$$

$$CaO + H_3PO_4 \qquad \rightarrow CaHPO_4 + H_2O$$

$$K_3PO_4 + H_2O \qquad \rightarrow KOH + K_2HPO_4$$

$$CaCl_2 + K_2HPO_4 \qquad \rightarrow CaHPO_4 + 2KCl$$

$$CaO + H_2O \qquad \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + 2CaHPO_4 \rightarrow Ca_3(PO_4)_2 + 2H_2O$$

From the above equations it is evident that the formation of dicalcium and tricalcium phosphate is entirely dependent upon the pH of the added phosphate solution. The reactions proceeding towards the formation of tribasic calcium phosphate seem to be favoured with the addition of a high pH phosphate. Tribasic calcium phosphate is more insoluble than dicalcium phosphate and this explains greater fixation from a more alkaline phosphate solution.

B. Basic Range. The main reaction that seems to have taken place in this range with the added phosphate leading to its fixation is with calcium hydroxide. The reactions might be translated into the following equational forms :—

$$Ca(OH)_2 + H_3PO_4 \qquad \rightarrow CaHPO_4 + 2H_2O$$

$$Ca(OH)_2 + NH_4H_2PO_4 \quad \rightarrow CaHPO_4 + 2H_2O + NH_3$$

$$Ca(OH)_2 + NH_4NaHPO_4 \rightarrow CaHPO_4 + H_2O + NaOH + NH_3$$

$$Ca(OH)_2 + (NH_4)_3PO_4 \quad \rightarrow CaHPO_4 + 2H_2O + 3NH_3$$

$$CaO + H_2O \qquad \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + 2CaHPO_4 \qquad \rightarrow Ca_3(PO_4)_2 + 2H_2O$$

The formation of tricalcium phosphate, therefore, results through the intermediate product, dibasic calcium phosphate. In view of the record of high fixation from phosphate solutions of higher pH and at higher pH range, the formation of tricalcium phosphate from alkaline phosphate solutions is not improbable.

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ADSORPTION OF PHOSPHATE ION BY INDIAN LIME (JABALPUR) AT DIFFERENT pH VALUES

PART II. EFFECT OF GLUCOSE AND HUMIC ACID

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ABSTRACT

Studies were made on the effect of glucose and laboratory prepared humic acid on the adsorbing capacity of a sample of Indian lime (Jabbalpur) at different pH values. It was noted that the presence of glucose and humic acid decreased the fixation of phosphate, the decrease being more marked in the case of humic acid. The pH of the systems also varied accordingly. It has been explained on the basis that the active surfaces are saturated and cemented in presence of organic matter, especially when humic acid is present, thus diminishing the association of phosphate with the adsorbent either physically or chemically.

The effect of organic ions on phosphate adsorption by lime has not been extensively studied. *En effet,* little work is available on this important aspect of study. Results of a few investigations are, however, recorded on the effect of these ions on phosphate adsorption in other systems. Most of the investigators have concluded that organic ions, in general, depress phosphate adsorption either by cementing the particles together or as in the case of minerals, by partially saturating the secondary valencies of the mineral lattice. In 1948, Coppenet and Boischot[1] reported desorption of phosphate adsorbed on the surface of calcium carbonate particles by the influence of the humic anion.

Because of the importance of the problem in the field of agriculture, it is felt that an attempt should be made to understand the dynamics of phosphate adsorption by lime in the presence of glucose and humic acid.

EXPERIMENTAL

Details of the procedure adopted for the present investigations have already been reported in paper I of this series.[2] For the studies in the presence of glucose and of humic acid, to the lime was added 1 gram of glucose or humic acid and then the solutions were added as described in part I and the experiments were repeated. The sample of glucose used was of B. D. H. AnalaR quality and humic acid was prepared in the laboratory from a good quality soil by the method described by Puri,[3]

TABLE 1

Adsorption of phosphate ion from H_3PO_4 (pH 3·8) by lime in presence of glucose at 30°C.

pH of HCl/NaOH added	Adsorption (mgm.)	pH (lime + HCl/NaOH)	pH of the mixture
(1)	(2)	(3)	(4)
4	0·0000	6·8	3·50
5	0·0000	7·1	3·70
6	0·0772	8·1	3·90
7	0·1390	8·3	4·10
8	0·2163	9·2	4·35
9	0·2935	10·6	4·50
10	0·6489	11·7	4·70

TABLE 2

Adsorption of phosphate ion from $NH_4H_2PO_4$ (pH 4·2) by lime in presence of glucose at 30°C

(1)	(2)	(3)	(4)
4	0·0000	6·8	4·95
5	0·0000	7·1	5·80
6	0·1236	8·1	6·50
7	0·2008	8·3	7·80
8	0·4326	9·2	9·10
9	0·6834	10·6	9·40
10	1·1896	11·7	10·30

TABLE 3

Adsorption of phosphate ion from NaH_2PO_4 (pH 5·6) by lime in presence of glucose at 30°C

(1)	(2)	(3)	(4)
4	0·0000	6·8	5·35
5	0·1699	7·1	5·90
6	0·2317	8·1	6·80
7	0·4944	8·3	7·40
8	0·7725	9·2	8·80
9	1·2205	10·6	9·00
10	2·7037	11·7	10·05

TABLE 4

Adsorption of phosphate ion from NH_4NaHPO_4 (pH 8·0) by lime in presence of glucose at 30°C

pH of HCl/NaOH added	Adsorption (mgm.)	pH (lime + HCl/NaOH)	pH of the mixture
(1)	(2)	(3)	(4)
4	0·2163	6·8	6·65
5	0·4171	7·1	6·75
6	0·5407	8·1	6·90
7	0·8806	8·3	7·35
8	1·4523	9·2	8·50
9	2·7192	10·6	9·75
10	5·3611	11·7	10·25

TABLE 5

Adsorption of phosphate ion from Na_2HPO_4 (pH 8·2) by lime in presence of glucose at 30°C

(1)	(2)	(3)	(4)
4	0·7879	6·8	6·75
5	1·3596	7·1	6·95
6	1·7149	8·1	7·30
7	1·8849	8·3	7·80
8	2·9200	9·2	8·75
9	5·1448	10·6	9·90
10	10·1970	11·7	10·40

TABLE 6

Adsorption of phosphate ion from $(NH_4)_3 PO_4$ (pH 8·4) by lime in presence of glucose at 30°C.

(1)	(2)	(3)	(4)
4	2·3329	6·8	7·75
5	4·0479	7·1	7·60
6	5·5311	8·1	7·80
7	5·9019	8·3	8·15
8	8·6211	9·2	9·05
9	10·1352	10·6	10·15
10	19·9459	11·6	10·65

TABLE 7

Adsorption of phosphate ion from Na_3PO_4 (pH 8·6) by lime in presence of glucose at 30°C

pH of NCl/NaOH added	Adsorption (mgm.)	pH (lime + HCl/NaOH)	pH of the mixture
(1)	(2)	(3)	(4)
4	4·9749	6·8	7·10
5	7·6632	7·1	7·70
6	10·7995	8·1	8·00
7	12·0201	8·3	8·25
8	17·2267	9·2	9·15
9	20·5176	10·6	10·25
10	24·3801	11·6	10·70

TABLE 8

Adsorption of phosphate ion from K_3PO_4 (pH 9·1) by lime in presence of glucose at 30°C

(1)	(2)	(3)	(4)
4	9·1618	6·8	7·50
5	15·1410	7·1	7·75
6	20·0077	8·1	8·20
7	23·1132	8·3	8·35
8	26·7285	9·2	9·50
9	27·7173	10·6	10·45
10	28·5979	11·6	10·80

TABLE 9

Adsorption of phosphate ion from H_3PO_4 (pH 3·8) by lime in presence of humic acid at 30°C.

(1)	(2)	(3)	(4)
4	0·0000	6·6	3·40
5	0·0000	6·9	3·60
6	0·0000	7·9	3·75
7	0·0772	8·1	4·00
8	0·1236	9·0	4·20
9	0·2008	10·4	4·40
10	0·5407	11·5	4·60

[154]

TABLE 10

Adsorption of phosphate ion from $NH_4H_2PO_4$ (pH 4·2) by lime in presence of humic acid at 30°C

pH of NCl/NaOH added	Adsorption (mgm.)	pH (lime + HCl/NaOH)	pH of the mixture
(1)	(2)	(3)	(4)
4	0·0000	6 6	4·75
5	0·0000	6·9	5·65
6	0·0000	7·9	6·40
7	0·1081	8 1	7 70
8	0·2626	9·0	8·95
9	0·4635	10·4	9·25
10	0·9579	11·5	10·20

TABLE 11

Adsorption of phosphate ion from NaH_4PO_4 (pH 5·6) by lime in presence of humic acid at 30°C

(1)	(2)	(3)	(4)
4	0·00C0	6·6	5·20
5	0·0000	6 9	5·75
6	0·1236	7·9	6·70
7	0·3399	8·1	7·30
8	0·6489	9·0	8·65
9	1·0042	10·4	8·85
10	2·6265	11·5	10·00

TABLE 12

Adsorption of phosphate ion from NH_4NaHPO_4 (pH 8·0) by lime in presence of humic acid at 30°C

(1)	(2)	(3)	(4)
4	0·0000	6·6	6·50
5	0·3090	6·9	6·65
6	0·3708	7·9	6·70
7	0·6489	8·1	7·20
8	1·1742	9·9	8·35
9	2·5029	10·4	9·60
10	5·1139	11·5	10·10

TABLE 13

Adsorption of phosphate ion from Na_2HPO_4 (pH 8·2) by lime in presence of humic acid at 30°C

pH of HCl/NaOH added	Adsorption (mgm.)	pH (lime + HCl/NaOH)	pH of the mixture
(1)	(2)	(3)	(4)
4	0·2626	6·6	6·40
5	0·5562	6·9	6·80
6	0·8961	7·9	7·15
7	1·4986	8·1	7·65
8	2·3638	9·0	8·70
9	4·8513	10·4	9·75
10	9·8262	11·5	10·30

TABLE 14

Adsorption of phosphate ion from $(NH_4)_3PO_4$ (pH 8·4) by lime in presence of humic acid at 30°C

(1)	(2)	(3)	(4)
4	0·7725	6·6	6·90
5	3·7080	6·9	7·50
6	4·6659	7·9	7·70
7	5·5620	8·1	8·00
8	7·9876	9·0	8·85
9	9·2854	10·4	9·90
10	19·1116	11·5	10·40

TABLE 15

Adsorption of phosphate ion from Na_3PO_4 (pH 8·6) by lime in presence of humic acid at 30°C

(1)	(2)	(3)	(4)
4	4·5268	6·6	6·95
5	7·0452	6·9	7·60
6	10·1506	7·9	7·90
7	11·2785	8·1	8·10
8	16·6551	9·0	9·00
9	19·8069	10·4	10·10
10	23·2368	11·5	10·55

TABLE 16

Adsorption of phosphate ion from K_3PO_4 (pH 9·1) by lime in
presence of humic acid at 30°C

pH of NCl/NaOH added	Adsorption (mgm)	pH (lime + HCl/NaOH)	pH of the mixture
(1)	(2)	(3)	(4)
4	8·4048	6 6	7·40
5	14·5539	6·9	7·60
6	19·4052	7·9	8·05
7	22·2171	8·1	8·20
8	25·9869	9·0	9·30
9	26·9448	10·4	10·25
10	27·7327	11·5	10·65

DISCUSSION

In part I[2], it has been shown that the addition of different acid/alkali solutions to lime resulted in each case an increase in pH of the mixtures due to the alkalinity of lime. It is evident from the experimental results presented above that this increase is less in presence of glucose and the increase is much less prominent in presence of humic acid. In general, the trend in the change of pH that was reported in part I with the addition of different phosphate solutions to the mixture of lime and aqueous HCl/NaOH, was also seen even when glucose and humic acid were added to the adsorbing system. For individual phosphates, adsorption increased with the increase of pH of HCl/NaOH and phosphate solutions. Again, no change in this basic trend of phosphate adsorption was found when the experiments were carried out in presence of glucose and humic acid. However, both of these substances reduced phosphate adsorption and this reduction was accompanied by a decrease in the resultant pH. When compared with the pH of the final solutions obtained from the addition of phosphates to the mixtures of calcium oxide and aqueous HCl/NaOH, this pH was found to be less. Humic acid reduced the resultant pH and also phosphate adsorption more than in the presence of glucose.

In the present study, it may also be noted that the extent of impediment in phosphate adsorption by lime in presence of glucose and humic acid considerably depends upon pH of aqueous HCl/NaOH and phosphate solutions. Incidentally, it may be mentioned here that our conjecture of surface reaction between phosphate and lime at lower pH values which has been reported in part I, was also based on the fact that little fixation could be found from acid phosphate solutions and at lower pH of HCl/NaOH, especially in presence of humic acid. Humic acid is well known for depressing phosphate fixation by saturating and cementing the active surfaces of the adsorbents. It is only towards the alkaline side (where the fixation of phosphate has been postulated to be due to chemical interaction) that the fixation is not negligible even in presence of humic acid. In all cases humic acid recorded a greater depressing effect than glucose perhaps as a result of greater cementing effect of the former than the latter. Further, the pH change brought about by each of these substances to the system of calcium oxide and aqueous HCl/NaOH added, showed

that humic acid reduced the pH of the solutions more than glucose. It may be easily conjectured that as a result of this reaction both of them depressed in varying degrees the formation of calcium chloride and calcium hydroxide (vide part I) by impeding the chemical reaction resulting to these substances either by saturating the surface of calcium oxide particles or making stable complexes with them, thus precipitating comparatively lesser amount of insoluble phosphates. The possibility of less surface reaction with phosphates due to the formation of their coatings on active calcium oxide surfaces can also be contemplated.

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A NOTE ON THE EFFECT OF GLUCOSE AND CANE SUGAR ON AMMONIUM NITRITE DECOMPOSITION

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Dhar and coworkers[1] have, in a number of experiments, shown that the nitrogenous fertilizers added to soil, undergo a series of changes in presence of sunlight and air, to form a highly unstable compound, ammonium nitrite which decomposes according to the following equation,

$$NH_4NO_2 = N_2 + 2H_2O + 718 \ Kcal.$$
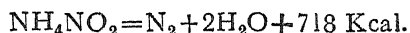
This phenomenon results in the decomposition and loss of the added nitrogenous fertilizer as free nitrogen gas. The loss has been found to be greater in light than in dark.

Dhar and Mukerjee[2] and Tripathi[3] and other workers have observed that the addition of carbonaceous substances to the nitrogenous fertilizers in soils considerably checks the loss of soil nitrogen. It has been suggested that the carbonaceous materials retard the rate of formation and decomposition of ammonium nitrite during ammonification, nitrification and nitrogen loss by photo-chemical process.

The present experiments cover the addition of cardonaceous substances like glucose and cane sugar in relation to the ammonium nitrite decomposition in presence of sunlight (decomposition in darkness has not been included in this paper). The quantities of carbonaceous materials used were so small (of the order of 0·1, 0·05 and 0·02 gm. per 100 c.c. of the solution) that they apparantly do not interfere with ammonium nitrite reactions, but only react as anti-catalysts in ammonium nitrite decomposition.

EXPERIMENTAL

Ammonium nitrite solution was prepared by mixing ammonium sulphate and sodium nitrite solutions so as to contain 1·2090, 0·6045 and, 0·3022 gs. of nitrogen per 100 c.c. of the solution. 100 c.c. of each solution was exposed to sunlight in Jena beakers covered with clean glass covers of uniform thickness.

Solutions of glucose and cane sugar were prepared by dissolving separately 0·10, 0·05 and 0·02 gs. of glucose and cane sugar in distilled water. These were added to ammonium-nitrite solutions prepared above and the volume was made upto 100 c.c.

The beakers containing the above solutions were exposed to sunlight for about six hours every day. The volume of the solutions was made up by adding distilled water at the close of the exposure every day. Temperature was recorded thrice every day by immersing the bulb of a thermmeter in a beaker of distilled water placed by the side of the exposed beakers. Thus, the temperature recorded is the mean of these values during the exposure.

Determination of total nitrogen[4], ammoniacal nitrogen[5] and nitrate nitrogen[6] was done by standard methods. Nitrite nitrogen was found out by substraction.

OBSERVATOINS

Period of exposure	...	125 hours	
Volume of ammonium nitrite solution	...	100 c.c.	
Average temperature	...	38·2° C,	

With ammonium nitrite solution

Total nitrogen added by ammonium nitrite in gms.	Total nitrogen left behind in gms.	Ammoniacal nitrogen left behind in gms.	Nitrite nitrogen left behind in gms.	Nitrate nitrogen formed in gms.	% of nitrate nitrogen formed	% loss of nitrogen
1·2090	0·7313	0·4207	0·2905	0·0201	1·662	39·51
0·6045	0·4070	0·2481	0·1421	0·0168	2·777	32·67
0·3022	0·2447	0·1503	0·0856	0·0088	2·911	19·01

With ammonium nitrite and glucose (0·1 gm.)

1·2090	0·8065	0·4304	0·3573	0·0188	1·555	33·29
0·6045	0·4835	0·2575	0·2088	0·0172	2·845	20·02
0·3022	0·2576	0·1421	0·1005	0·0090	2·978	15·75

With ammonium nitrite and cane sugar (0·1 gm.)

1·2090	0·7861	0·3782	0·3878	0·0201	1·662	34·98
0·6045	0·4563	0·2391	0·2074	0·0098	1·124	24·52
0·3022	0·2489	0·1429	0·1008	0·0052	1·721	17·63

With ammonium nitrite and glucose (0·05 gm.)

1·2090	0·7758	0·4207	0·3360	0·0191	1·579	35·83
0·6045	0·4667	0·2488	0·2030	0·0149	2·465	22·79
0·3022	0·2564	0·1413	0·1069	0·0082	2·713	15·15

With ammonium nitrite and cane sugar (0·05 gm.)

1·2090	0·7583	0·3715	0·3676	0·0192	1·595	37·28
0·6045	0·4394	0·2319	0·1986	0·0089	1·472	27·32
0·3022	0·2452	0·1382	0·1023	0·0047	1·555	18·86

With ammonium nitrite and glucose (0·02 gm.)

1·2090	0·7687	0·4112	0·3374	0·0201	1·662	36·42
0·6045	0·4512	0·2487	0·1880	0·0145	2·398	25·36
0·3022	0·2539	0·1399	0·1077	0·0063	2·084	15·99

With ammonium nitrite and cane sugar (0·02 gm.)

1·2090	0·7474	0·3604	0·3682	0·0188	1·561	38·19
0·6045	0·4371	0·2488	0·1783	0·0100	1·654	27·69
0·3022	0·2448	0·1354	0·1019	0·0075	1·482	18·98

DISCUSSION

Dhar's theory of photo-nitrification of nitrogenous fertilizers postulates the formation of an unstable compound through a series of chemical reactions in soil, which decomposes in the presence of sunlight (auto-catalyst) and air into nitrogen gas as under,

$$NH_4NO_2 = N_2 + 2H_2O + 7.18 \text{ Kcal.}$$
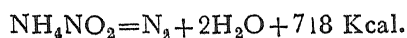
This loss of nitrogen from soil, due to the decomposition of the fertilizer can be appreciably reduced by addition of carbohydrates or cellulosic materials to the soil. Dhar and Mukherjee[7] and Tripathi and Banerjee[8] have observed that the addition of glucose, molasses or sugar retards the rate of nitrogen loss from the soils containing nitrogenous fertilizers. These observations lead to the conclusion that the formation and decomposition of ammonium nitrite in solution can be effectively checked by the addition of corbohydrates to it. In the present experiments, ammonium nitrite solution containing 1.2090, 0.6045 and 0.3022 gms. of it per 100 c.c. of the solution, after exposure to sunlight at an average temperature of 38.2°C, lost 39.51%, 32.67% and 19.01% of nitrogen respectively, after a period of 125 hours. But in presence of glucose or cane sugar, the loss of nitrogen from ammonium nitrite solution under the same conditions of the experiment was observed to be considerably less. Thus, the above loss of nitrogen in ammonium nitrite solution with glucose and cane sugar is reduced as recorded below.

Ammonium Nitrite		Glucose		Cane Sugar	
Quantity	% loss of nitrogen	Quantity	% loss of nitrogen	Quantity	% loss of nitrogen
1.2090	39.51	0.10 gm.	33.29	0.10 gm.	34.98
1.2090	...	0.05 gm.	35.83	0.05 gm.	37.28
1.2090	...	0.02 gm.	36.42	0.02 gm.	38.19
0.6045	32.67	0.10 gm.	20.02	0.10 gm.	24.52
0.6045	...	0.05 gm.	22.79	0.05 gm.	27.32
0.6045	...	0.02 gm.	25.36	0.02 gm.	27.69
0.3022	19.01	0.10 gm.	14.75	0.10 gm.	17.63
0.3022	...	0.05 gm.	15.15	0.05 gm.	18.86
0.3022	...	0.02 gm.	15.99	0.02 gm.	18.98

The following conclusions are drawn from the observations:

(1) With the higher concentration of ammonium nitrite, the loss of nitrogen is greater.

(2) The higher concentration of glocuse and/or cane sugar show greater efficiency in retarding nitrogen loss, i. e. the decomposition of ammonium nitrite.

(3) Oxidation of nitrite into nitrate is appreciable, which was decomposed and lost as ammonium nitrite.

(4) Nitrite part of ammonium nitrite suffers greater loss than ammonium part.

Studies of such reactions with other such anti catalysts, both in light and dark are in progress.

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EFFECT OF SALTS ON THE RELEASE OF ADSORBED UREA BY SOILS

By

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ABSTRACT

Urea adsorbed by the soil can be released by the application of NaCl, KCl, CaCl$_2$ and Na$_2$HPO$_4$ Practically all the adsorbed urea from dilute solutions can be lost by leaching action in presence of small amounts of Na, K and Ca ions.

In a previous communication[1], we reported adsorptive capacities of soils, clay minerals and oxides of iron and aluminium for urea from its dilute solutions. No attempt was made to find out the fate of adsorbed urea by the materials. In the present studies, the salts have been used to release the adsorbed urea by a soil.

EXPERIMENTAL

The soil used in these experiments was collected from Allahabad University, Chemistry Department Campus. The soil was finely powdered and passed through a 100 mesh sieve. After oven-drying, it was stored in a stoppered bottle and used for adsorption expriments.

5 gms. of the soil was taken in 250 ml. conical flasks and 50 ml. of urea solution of 0·1 M, 0·05 M, 0·0333 M concentration were added to each flask. The contents were shaken for one hour after corking the flasks. Next day, the supernatant liquid was separated by filtering it through a Buchner funnel using suction. The soil on the funnel was washed thoroughly with distilled water to free it of remaining urea. Then the soil with the filter paper was transferred to the conical flasks and shaken with 50 ml. of 0·1 M and 0·05 M solutions of NaCl, KCl, CaCl$_2$ and Na$_2$HPO$_4$ respectively. Next day, the filtrates were analysed for urea contents, using sodium hypobromite method.[2] The amount of urea found out denotes the amount of urea released by salt treatment. The original solutions were also analysed for their urea contents. The adsorbed urea was found out by difference in the concentration of urea before and after the adsorption.

The soil used in these experiments contained 0·6045% carbon and 2·8% calcium oxide. Its pH was 8·4.

TABLE 1

Effect of KCl on the release of adsorbed urea

Concentration of urea used	gms. of urea adsorbed by 5 gms. of soil	gms. of urea released by 5 gms. of urea-treated soil using	
		0·1M KCl	0·05 M Kcl
0·1M	0·03661	0·03221	0 02196
0·05M	0·01464	0·01757	0·01318
0·033M	0·01171	0·01175	0·00732

TABLE 2

Effect of NaCl on the release of adsorbed urea

Concentration of urea used	gms. of urea adsorbed by 5 gms. of soil	gms. of urea released by 5 gms. of urea-treated-soil using	
		0·1M NaCl	0·05 NaCl
0·1M	0·03661	0·03601	0·02929
0·05M	0·01464	0·01903	0·01757
0·033M	0·01098	0·01464	0·01318

TABLE 3

Effect of CaCl₂ on the release of adsorbed urea

Concentration of urea used	gms. of urea adsorbed by 5 gms. of soil	gms. of urea released by 5 gms. of urea-treated-soil using	
		0·1M CaCl₂	0·05M CaCl₂
0·1M	0·03661	0·03515	0·02444
0·05M	0·01464	0·01464	0·00878
0·033M	0·01098	0·00732	0·00

TABLE 4

Effect of Na₂HPO₄ on the release of adsorbed urea

Concentration of urea used	gms. of urea adsorbed by 5 gms. of soil	gms. of urea released by 5 gms. of urea-treated-soil using
		0·1M Na₂HPO
0·1M	0·03661	0·02489
0·05M	0·01464	0·01175
0·033M	0·01171	0·00585

[164]

DISCUSSION

A perusal of the above results shows clearly that the absorbed urea can be extracted from the soil by using salt solutions of varying concentrations. The order in which the salts used displace adsorbed urea varies with the amount of urea adsorbed. The higher concentrations of the salts release greater amounts of adsorbed urea whilst the less concentrated salts release less of urea. However, practically all the urea adsorbed from less concentrated solutions of urea, is released by the salt solutions used, in comparison to the urea adsorbed by the soil from concentrated urea solution i. e. 0·1 M solution.

It is interesting to note that the release of urea from soil samples treated with 0·05M and 0·033M solution of urea, release more of urea than the amount adsorbed. This shows that some ammonium ions are also being released as a result of salt-treatment, which are being determined by the hypobromite method. This takes place due to base-exchange process in the soil. Na^+, K^+ and Ca^{++} ions release NH_4^+ ions from the soil.

The release of adsorbed urea by the salt solutions can be explained by assuming that urea is adsorbed in such a manner that it is easily exchangeable and Na^+, K^+ and Ca^{++} ions displace the adsorbed urea. Also, it is possible that during adsorption urea gets transformed into ammonium ions and is adsorbed by the soils which can be released later by base-exchange.

The presence of the cations, thus, greatly helps in releasing the adsorbed urea The leaching losses of urea can be, in this way, increased by different fertilizing practices.

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STUDIES ON THIOARSENATES

PART II : A POTENTIOMETRIC AND CONDUCTOMETRIC STUDY

By

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ABSTRACT

The interaction between arsenate and hydrosulphide (NaHS) has been shown to proceed in a number of steps forming thioxy and thioarsenates, *viz.*; Na_3AsSO_3, $Na_3AsS_2O_2$, Na_3AsS_3O, and Na_3AsS_4. In alkaline medium the reaction is ionic in nature, and OH^- ions are released at every step of the reaction. Further the reactions being reversible and slow, they are never complete in alkaline medium, so that very few OH^- ions actually exist in the free state in the solutions. On adding acids the reaction proceeds to completion forming thioarsenate anions. Further, the increase in hydrogen ion concentration suppresses the dissociation of the thioacid, forming molecular H_3AsS_4, which decomposes, rather slowly, to give a precipitate of As_2S_5 and liberates H_2S. It has further been suggested that, in general, with the increased number of sulphur atoms in the molecules of various thioxy and thioarsenic acids, the acids become stronger.

In part I of this paper[1] various factors determining the precipitation of arsenic pentasulphide by decomposing its thiosalt with HCl have been studied. The present paper deals with a physico-chemical study of the thioxy and thioarsenates, their formation and decomposition by acids, leading to the precipitation of As_2S_5.

It has been found that as with the arsenite the reaction occurs in steps forming thioxy and thioarsenates, and arsenic pentasulphide is precipitated from the thiocompound, owing to the decomposition of thioarsenic acid molecules. From monosulphoxyarsenic acid (H_3AsSO_3) however, only sulphur separates. It is further observed that in this case the reactions are rather slow, and the formation of thioarsenate is never complete in alkaline solutions.

RESULTS AND DISCUSSION

Formation of thioxy and thioarsenates

(a) pH measurements (by Univariant method):

In this set of experiments a fixed volume of $0.2M$ $Na_2HAsO_4 . 7H_2O$ solution was mixed with varying amounts of $0.2M$ NaHS solution and the total volume was raised to 50 c.c. in each case. The pH of these solutions was measured with a Cambridge pH meter (Senstivity 0.02 units) using glass electrodes. The pH of

NaHS solution alone of similar concentrations was also noted for comparision. The results are graphically represented in Fig. 1, which shows that :–

(i) The pH of these solutions goes on increasing with the addition of NaHS, finally the curve tending to become constant, after 4 equivalents of NaHS have been added.

(ii) The hydrolysis of the complex thioxy and thioarsenates is lesss than that of NaHS.

Fig. 1

(I)▲ NaHS alone (for 5 c.c.)
(II)✕ " " (for 2 c.c.)
(I)● 5 c.c. of 0·2 M Na₂HAsO₄ + NaHS
(II)⊙ 2 c.c. " " " " + " "
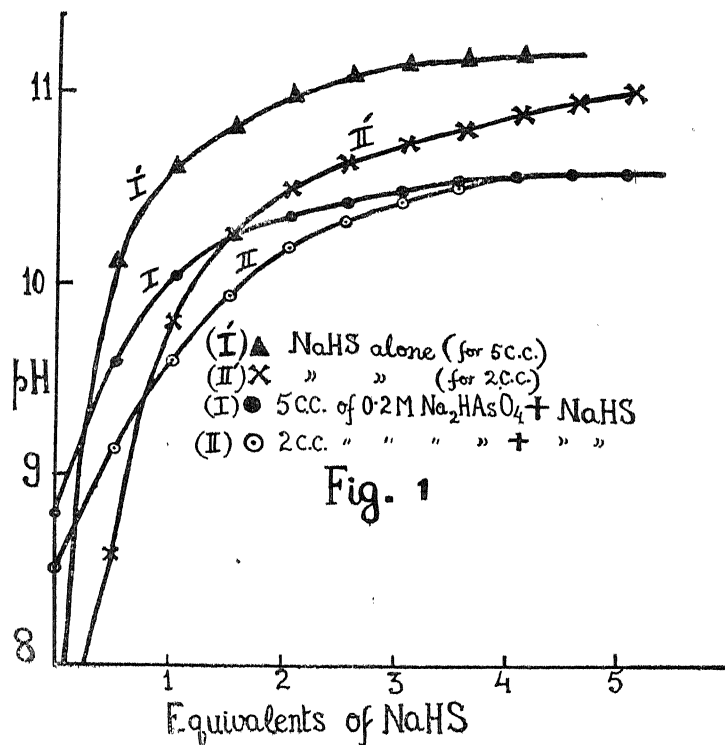
(b) Conductivity Measurements (by Differential Univaraiant method) :

A fixed volume of arsenate solution was mixed with varying amounts of NaHS solution, and the total volume raised to 50 c.c. The conductance of these solutions was measured at 32·5±0·1°C by a L. N. Kohlrausch slide wire with an audiofrequency oscillator. The conduct ance values for corresponding amounts of NaHS alone were also determined. The observed conductance of these solutions was substracted from the sum of the conductance of arsenate and NaHS solutions. The results are given in Fig. 2, in which the differences between the observed conductance and the sum of the conductance of arsenate and NaHS solutions have been plotted against the NaHS added.

Fig. 2 shows that the slope of the curves changes with each addition of NaHS. Finally the curves tend to be constant, after four equivalents of NaHS have been added. It thus indicates the stepwise formation of thioxy and thioarsenates viz., Na_3AsSO_3, $Na_3AsS_2O_2$ Na_3AsS_3O and Na_3AsS_4 with the progressive addition of NaHS to arsenate solution.

A standard 0·1 M sodium arsenate solution (2 c.c.) was mixed with increasing amounts (2, 4, 6 and 8 c.c.) of 0·1M NaHS solution. The thioxy and thioarsenates
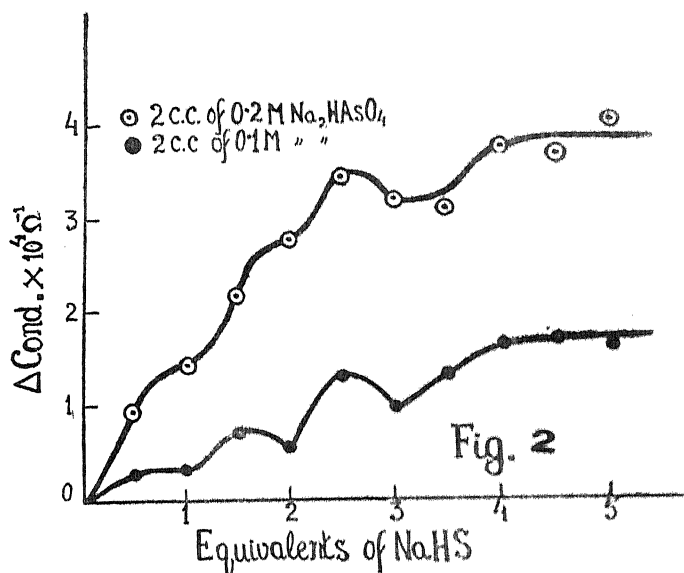
so formed were acidified with varying amounts of 0·1 M HCl solution and pH and conductance of the solutions measured. The total volume was kept 50 c.c. in each case. The results are given in figs. 3-4.
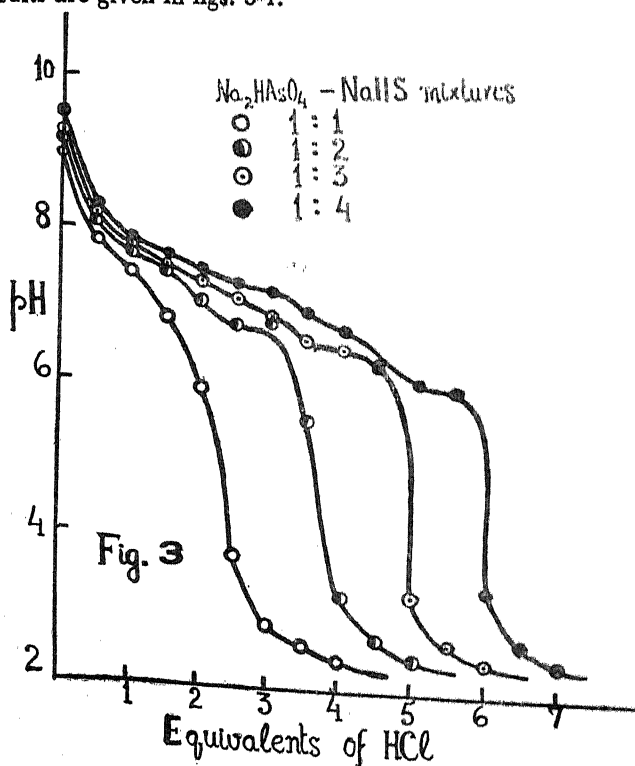
Fig. 3 shows the pH titration curves of thioxy and thioarsenates. In it the first curve (As: NaHS = 1: 1) has only one well marked inflexion. The second and third curves corresponding to (As: NaHS = 1 : 2 and 1 : 3 respectively) have two and the fourth curve (As: NaHS=1: 4) has three inflextions.
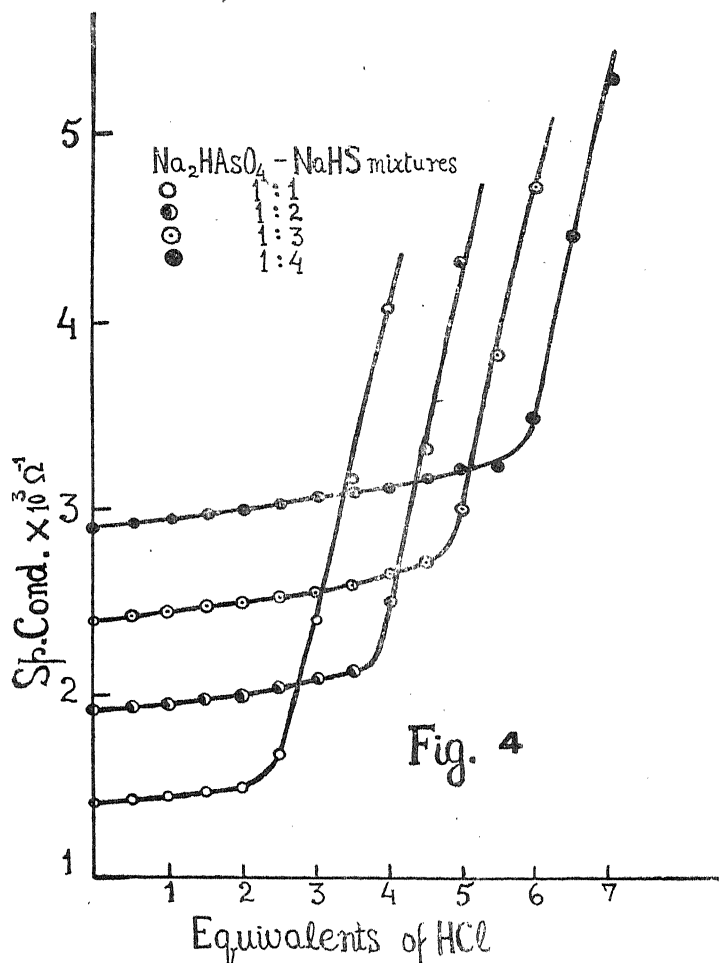
Fig. 4

The conductometric titration curves (fig. 4) show that at first the conductance increases very slowly in all cases, till the acid added is equivalent to the sodium present in the solutions. Finally the curves rise steadily, as is the case for the conductometric titration of a weak base with a strong acid.

The Results recorded here, thus show that the reaction between arsenate and hydrosulphide occurs in a number of steps, involving a seris of stepwise equilibria, as suggested below:—

$$AsO_4^{3-} + HS^- \rightleftharpoons AsSO_3^{3-} + OH^-$$
$$AsSO_3^{3-} + HS^- \rightleftharpoons AsS_2O_2^{3-} + OH^-$$
$$AsS_2O_3^{3-} + HS^- \rightleftharpoons AsS_3O^{3-} + OH^-$$
$$AsS_3O^{3-} + HS^- \rightleftharpoons AsS_4^{3-} + OH^-$$

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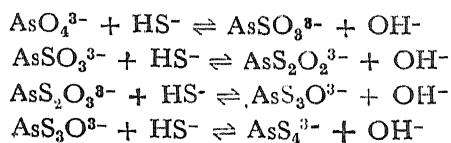
It will be seen from above that OH- ions are released at every step of the reaction, *i.e.* with increasing acidity of the medium the formation of AsS_4^3 would be enhanced. It appears, however, that very few OH- ions do actually exist in the free state in these solutions, so that on adding acid to them, the conductometric titration curves (fig. 4) do not show any initial fall, but go on rising very slowly from the very begining. It happens so because all these reactions being reversible in nature, much of the reactions is not completed in alkaline medium. On adding acid, the OH- ions are consumed from the system, so that the reaction proceeds towards the right side, finally giving the thioarsenate anions. Further, the increase in hydogen ion concentration suppresses the dissociation of the thio acid, forming thioarsenic acid molecules, which really decompose, rather slowly, to give a precipitate of arsenic pentasulphide and liberating H_2S.

Half neutralization Points:

By an analysis of the pH titration curves (Fig. 3) the following half neutralization points of the various thioxy and thioarsenic acids are obtained.

TABLE 1

Acid	pH at half neutralization points		
	I	II	III
H_3AsSO_3	3·70	6·82	7·86
$H_3AsS_2O_2$	5·60	6·75	7·44
H_3AsS_3O	6·30	6·56	7·10
H_3AsS_4	5·96	6·24	6·92

A persual of the above table shows that with the increase in the number of sulphur atoms in the molecules of various thioxy and thioarsenic acids, the second and third half neutralization points are obtained at a lower pH value. These certainly show that the acids become stronger. In the first case, however, this sequence is not maintained, because a solution of H_3AsSO_3 precipitates only sulphur, whilst others decompose to give arsenic pentasulphide; and thus the whole sequence is disturbed. Further these data cannot be employed to calculate the dissociation constant of these acids. It is noted that the pH curves are pushed upwards with time, so much so that the first half neutralization point of thioarsenic acid (prepared by mixing arsenate and NaHS solutions in the ratio of As:S 1:4 and adding HCl) comes out to be at pH 5·96, higher than that obtained in the case of thioarsenious acid[2] (pH 5·40 table 2), whilst thioarsenic acid is well known to be a stronger acid[3]. The second and third half neutralization points are, however, in the natural sequence in all cases, as will be evident by a comparision of the results of table 1 with the half neutralization points[2] of thioxy and thioarsenious acids given below in table 2,

TABLE 2

	pH at half neutralization points		
	I	II	III
H_5AsSO_3	7·25	10·12	11·35
$H_5AsS_2O_2$	6·75	9·60	11·02
H_5AsS_3O	5·48	7·00	10·68
H_5AsS_4	5·40	6·35	7·90

This discrepency may be attributed to the following two facts:—

(1) The formation of thioarsenate liberates more alkali than that released in the formation of thioarsenite as represented below:—

$$Na_2HAsO_3 + 4NaHS = Na_5AsS_4 + NaOH + 2H_2O$$

$$Na_2HAsO_4 + 4NaHS = Na_3AsS_4 + 3NaOH + H_2O$$
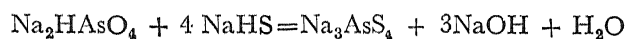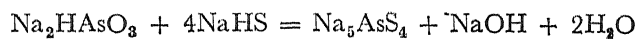
(2) The steps suggested in the formation of thioarsenate are slow. Hence in the titration OH⁻ ions are simultaneously released, and this vitiates the results.

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(3) *vide* Mellor : *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 1929, Vol. IX, p. 315.

ON STRONG SUMMABILITY OF FOURIER SERIES AND ITS CONJUGATE SERIES

By

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1. Let $f(x)$ be a function of x integrable (L) over $(-\pi, \pi)$ and be periodic with period 2π. Let its Fourier series be

$$(1.1) \qquad \tfrac{1}{2} a_0 + \sum_{n=1}^{\infty} (a_n \cos nx + b_n \sin nx)$$

The conjugate series of (1.1) is

$$(1.2) \qquad \sum_{n=1}^{\infty} (b_n \cos nx - a_n \sin nx)$$

We denote by $s_n(x)$ and $\bar{s}_n(x)$ the partial sums of the series (1.1) and (1.2) respectively.

We write

$$\phi(t) = \phi(t, x) = \tfrac{1}{2} [f(x+t) + f(x-t) - 2s],$$
$$\psi(t) = \psi(t, x) = \tfrac{1}{2} [f(x+t) - f(x-t)].$$

Let

$$\bar{f}_n = f_n(x) = \frac{1}{\pi} \int_{1/n}^{\pi} \psi(t). \cot \frac{t}{2} \, dt,$$

and put

$$(1.3) \qquad \bar{f}(x) = \lim_{n \to \infty} \bar{f}_n(x)$$

whenever the latter exists.

A series Σa_n, with partial sums s_n is said to be strongly summable with the index 2 to the sum s, or summable H_2, if there exists a finite s such that

$$\sum_{v=0}^{n} | s_v - s |^2 = o(n)$$

The strong summability of Fourier series and its conjugate series has been discussed by a number of writers like Hardy and Littlewood (1913; 1926; 1935), Fejér (1938), Carleman (1923) Sutton (1925), Szász (1940), Marcinkiewicz (1939), Wang (1944; 1945) and U. N. Singh (1946).

[172]

For the Fourier series Wang [7] proved the following theorem.

Theorem A. If

$$\int_0^t |\phi(u)|\, du = o\left[\frac{t}{(\log \frac{1}{t})^\alpha}\right], \text{ as } t \to 0,$$

for some $\alpha > \frac{1}{2}$, then (1.1) is summable H_2 to the sum s.

Analogous theorem for the conjugate series (1.2) has been proved by Singh [8] as follows.

Theorem B. If

$$\int_0^t |\psi(u)|\, du = o\left[\frac{t}{(\log_{1/t})^\alpha}\right], \text{ as } t \to 0$$

for some $\alpha > \frac{1}{2}$, then the series (1.2) is summable H_2 to $\bar{f}(x)$ provided that the limit (1.3) exists.

The object of this paper is to extend the scope of these theorems. I shall show that these theorems are the special cases of the theorems 1 and 2 proved here.

I prove the following theorems.

Theorem 1. *If*

$$\int_0^t |\phi(u)|\, du = o[\, t\, K(t)\,], \text{ as } t \to 0$$

where $K(t)$ is a positive function of t, such that

(i) $K(t) \to 0$, as $t \to 0$,

ii) $K(t)$ is monotonic in $(0, \delta)$,

(iii) $\displaystyle\int_0^\delta \frac{K^2(t)}{t}\, dt = O(1)$

where δ is small but fixed, then the series (1.1) is summable H_2 to the sum s.

[173]

Theorem 2. *If*

$$\int_0^t | \psi(u) | \, du = o\left[t \, K(t) \right], \text{ as } t \to 0,$$

where $K(t)$ is as in Theorem I, then the series (1.2) is summable H_2 to $f(x)$ provided that the limit (1.3) exists.

I am deeply indebted to Professor B. N. Prasad for his kind help and advice in the preparation of this paper.

2. I shall need the following lemmas to prove the theorems.

Lemma 1 [7]   If

$$\int_0^t | \phi(u) | \, du = o(t), \text{ as } t \to 0$$

then

$$\sum_{v=0}^{n} | s_v - s |^2 = \frac{4}{\pi^2} \int_{1/n}^{\delta} \frac{\phi(t)}{t^2} \, dt \int_{1/u}^{t} \phi(u) . \frac{\operatorname{Sin} n(u-t)}{u-t} \, du + o(n)$$

where δ is small but fixed.

Lemma 2 [8]   If

$$\int_0^t | \psi(u) | \, du = o(t), \text{ as } t \to 0$$

then

$$\sum_{v=1}^{n} | \bar{s}_v - \bar{f}_n(x) | = \frac{4}{\pi^2} \int_{1/n}^{\delta} \frac{\psi(t)}{t^2} \, dt \int_{1/n}^{t} \psi(u) \frac{\operatorname{Sin} n(u-t)}{u-t} \, du + o(n)$$

where δ is small but fixed.

3. PROOF OF THEOREM 1

Since $K(t) \to 0$, as $t \to 0$ under the hypothesis (i), $\int_0^t | \phi(u) | \, du = o(t)$

[174   ]

Hence by Lemma I, we have

$$(3.1) \quad \sum_{v=0}^{n} |s_v - s|^2 = \frac{4}{\pi^2} \int_{1/n}^{s} \frac{\phi(t)}{t^2} dt . \int_{1/n}^{t} \phi(u) \frac{\operatorname{Sin} n(u-t)}{u-t} du + o(n),$$

It follows from the hypothesis that

$$\int_{1/n}^{t} \phi(u) . \frac{\operatorname{Sin} n(u-t)}{u-t} du = O\left[\int_{1/n}^{t} |\phi(u)| n \, du \right]$$

$$= O[n . o \{ t . K(t) \}]$$

$$= o[n \, t \, K(t)]$$

Hence we get

$$(3.2) \int_{1/n}^{\delta} \frac{\phi(t)}{t^2} du \int_{1/n}^{t} \phi(u) \frac{\operatorname{Sin} n(u-t)}{u-t} du = o\left[n \int_{1/n}^{\delta} \frac{K(t)}{t} |\phi(t)| \, dt \right]$$

If now $\quad \Phi(t) = \int_{0}^{t} |\phi(u)| \, du$, then we have

$$(3.3) \int_{1/n}^{\delta} \left| \frac{\phi(t)}{t} \right| K(t) \, dt = \left[\Phi(t) . \frac{K(t)}{t} \right]_{1/n}^{\delta} - \int_{1/n}^{\delta} \Phi(t) . \frac{K'(t)}{t} dt + \int_{1/n}^{\delta} \Phi(t) . \frac{K(t)}{t^2} dt,$$

$$= O(1) + O\left[\int_{1/n}^{\delta} |K(t) . K'(t)| \, dt \right] + O\left[\int_{1/n}^{\delta} \frac{K^2(t)}{t} dt \right],$$

By hypothesis (ii) K (t) is monotonic, so its differential coefficient is of constant sign.

Hence we have

$$O\left[\int_{1/n}^{\delta} |K^2(t) K'(t)| \, dt \right] = O\left[\left| \int_{1/n}^{\delta} \frac{1}{3} \frac{d}{dt} (K^3(t)) \, dt \right| \right]$$

$$= O\left[\left\{ K^3(t) \right\}_{1/n}^{\delta} \right]$$

$$= O(1)$$

[175]

Also by hypothesis (*iii*)

$$O\left[\int_{1/_n}^{\delta} \frac{K^2(t)}{t}\,dt\right] = O(1)$$

Hence we have

$$(3.4)\quad \int_{1/_n}^{\delta} |\phi(t)|\,\frac{K(t)}{t}\,dt = O(1)$$

The theorem follows from (3.1), (3.2), and (3·4).

4. The proof of theorem 2 is similar to that of theorem 1.

5. Now we see that the theorems A and B are the special cases of Theorems 1 and 2 respectively. Because in these theorems $K(t) = \dfrac{1}{\left(\log \frac{1}{t}\right)^{\alpha}}$ which is positive tends

to zero with t and is monotonic in $(0, \delta)$ also

$$\int_{0}^{\delta} \frac{K^2(t)}{t}\,dt = \int_{0}^{\delta} \frac{1}{t}\,\frac{dt}{(\log \,^{1/}t)^{2\alpha}}$$

$$= \int_{\log \,^{1/}\delta}^{\infty} \frac{dx}{x^{2\alpha}}$$

$$= O(1), \text{ since } \alpha > \tfrac{1}{2},$$

All the conditions are satisfied, hence the theorems follow.

6. It can be seen that the conditions on $K(t)$ are satisfied even if we take

$$(a)\quad K(t) = \frac{1}{\left(\log\frac{1}{t}\right)^{1/2}\left(\log\log \,^{1/}t\right)} \qquad\qquad \alpha > \tfrac{1}{2},$$

$$(b)\quad K(t) = \frac{1}{\left(\log \,^{1/}t \log\log\frac{1}{t}\right)^{1/2}\left(\log\log\log\frac{1}{t}\right)^{a}} \qquad\qquad \alpha > \tfrac{1}{2},$$

$$(c)\quad K(t) = \frac{1}{\left(\log\frac{1}{t}\log\log\frac{1}{t}\log\log\log\frac{1}{t}\right)^{1/2}\left(\log\log\log\log\frac{1}{t}\right)^{a}} \qquad \alpha > \tfrac{1}{2}$$

and so on.

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STUDIES ON THIOMOLYBDATES

PART I: PRECIPITATION OF MOLYBDENUM SULPHIDE

By

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ABSTRACT

The precipitation of molybdenum sulphide by decomposing its thiosalt with acids has been studied. It has been shown that molybdenum is completely precipitated only when the amounts of added NaHS is sufficient to give a ratio of Mo:S = 1:8, and so much of acid is added as may completely displace all the sodium present there in the system. Further molybdenum has been shown to precipitate with more sulphur than which conforms to the formula MoS_3 possibly having a composition $3MoS_3.H_2S.H_2O$.

In previous communications[1,2] from this laboratory results on the study of thioarsenites and thioarsenates have been reported. The present paper deals with a similar study on thiomolybdates.

In has been found that molybdeum sulphide is completely precipitated from a molybdate solution by decomposing its thiosalt with acid, when the amount of sulphur added as hydrosulphide is sufficient to give a ratio of Mo:S 1:8 in the system, a value much higher than that required to form MoS_3. Further, molybdenum has been shown to be precipitated with more sulphur than which conforms the formula MoS_3, possibly having a composition $3MoS_3.H_2S.H_2O$.

EXPERIMENTAL

A 0·25 M stock solution of sodium molybdate ($Na_2MoO_4.2H_2O$) was prepared and standardized by precipitating molybdenum as oxinate[3] and lead molybdate[4]. The reagent NaHS was prepared as usual.

Precipitations by varying amounts of NaHS:—

A standard 0·025 M sodium molybdate solution (10 c.c.) was treated with varying amounts of 0·05 M NaHS solution, and acidified with equal volumes of 2N hydrochloric acid. The precipitates thus obtained were filtered through weighed sintered glass crucibles (G-4) washed thoroughly with water alcohol and ether successively, dried at the filter pump by suction and then in a vacuum desiccator and finally weighed.

The results given below (table 1) show that molybdenum is completly precipitated when Mo:S=1:8 in the system.

TABLE 1

0·05 NaHS added (c.c.)	2N HCl added (c.c.)	Amounts ppted (g.)
5	15	0·0080
10	20	0·0178
15	25	0·0290
20	30	0·0360
25	35	0·0442
30	40	0·0474
35	45	0·0504
40	50	0·0522
45	55	0·0520
50	60	0·0524

Precipitations by varying amounts of HCl :

In this set of experiments, the solution containing thiomolybdate (10 c.c. of 0·025 M sodium molybdate + 20 c.c. of 0·1 M NaHS) were acidified with varying amounts of 0·05 M HCl and left overnight. 2 c.c. of 1% $BaCl_2$ solution was also added in each case to coagulate the precipitates completely. The precipitates thus obtained were filtered through weighed sintered glass crucibles (G. 4) washed thoroughly with water, alcohol and ether and weighed after suitable treatment. The final pH of these solutions was also noted. The results are given in Table 2.

TABLE 2

0·05 HCl added (c.c.)	pH	Amounts ppted (g)
40	5·80	0·000
42	5·32	0·000
45	4·52	0·0260
46	4·46	0·0366
47	4·32	0·0518
48	4·20	0·0544
49	3·68	0·0576
50	3·18	0·0550
52	2·85	0·0530
55	2·65	0·0570

Table 2 shows that molybdenum sulphide is precipitated when about 9 equivalents of HCl have been added, i. e. when only one sodium is left unneutralized. But there is also large amount of adsorption of Ba^{++} ions under such conditions, so that the results obtained are not in any definite order.

Composition of molybdenum sulphide ppt :

The percentage of molybdenum in the precipitates of molybdenum sulphide, as calculated from table 1, is 45·93. It suggests the formulae :

$$MoS_3.H_2O, \quad 2MoS_3.H_2S, \quad \text{or} \quad 2MoS_2.S \quad \text{with of Mo as } 45\cdot71, 45\cdot93 \text{ and } 46\cdot15\%$$

respectively.

Taimni and Agarwal[5] have however given the formula of the precipitate to be $MoS_3.2H_2O$. Feigl[6] reports that molybdenum precipitates with more sulphur than required by the formula MoS_3, possibly as $MoS_3.S_2$. It was therefore considered desirable to determine sulphur in the precipitates of molybdenum sulphide. Sulphur was oxidised by bromine (CCl_4 sol.) and conc. nitric acid. Drastic treatment was required to get molybdenum sulphide in solution. It was then precipitated and estimated as barium sulphate. The results are given in table 3.

TABLE 3

Amounts of sulphide ppt taken g.	wt. of the ppt $BaSO_4$ g.	Sulphur Calc. g.	%
0·0990	0·3654	0·0501	50·64
0·1258	0·4648	0·0638	50·75

This suggests a formula $3MoS_3.H_2S.H_2O$ containing $S = 50\cdot93\%$, and $Mo = 45\cdot85\%$. It closely agrees with the experimental results.

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STUDIES ON THIOMOLYBDATES

PART II. A PHYSICO-CHEMICAL STUDY OF THEIR FORMATION AND DECOMPOSITION

By

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ABSTRACT

The reaction between molybdate and NaHS has been shown to proceed through a set of ionic reversible reactions, forming a series of thioxy and thiomolybdate compunds. The special feature of this reaction is that molybdenum forms a number of thiosalts, *viz.*; Na_2MoS_1, $Na_4H_2MoS_6$ and $Na_8H_4MoS_8$; but molybdenum is completely precipitated only from the thiomolybdate $Na_6H_4MoS_8$. Further, in alkaline medium the reactions are never complete, and the formation of thiomolybdic is favoured by the increasing acidity of the medium, which also suppresses the dissociation of thiomolybdic acid, forming $H_{10}MoS_8$ molecules, which decompose to give a precipitate of molybdenum sulphide and H_2S. Before molybdenum is precipitated it also gives two coloured thioanions $(H_6MoS_8)^{4-}$ and $(H_8MoS_8)^{2-}$ having yellow and orange red colour respectively.

In part I[1] the precipitation of molybdenum sulphide has been studied, and it has been observed that precipitation occurs in the acid medium, due to the decomposition of thiomolybdic acid. The present paper deals with the physico-chemical study on the formation of thioxy and thiomolybdates, and their decomposition by acids precipitating molybdenum sulphide.

It has been found that the reaction between molybdate and NaHS occurs in a number of steps, forming a series of thioxy and thiomolybdate compounds. The special feature of this reaction is that molybdate forms a number of thiosalts viz. Na_2MoS_4, $Na_4H_2MoS_6$, and $Na_6H_4MoS_8$, but molydenum is completely precipitated only by decomposing the thiomolybdate $Na_6H_4MoS_8$ with acid. Further before molybdenum is precipitated, it gives two coloured thio anions $(H_6MoS_8)^{4-}$ and $(H_8MoS_8)^{2-}$ having yellow and orange red colour respectively.

RESULTS AND DISCUSSION

Formation of thioxy and thiomolybdates :—

(A) pH measurements :

A solution of 0·05 M sodium molybdate (2 c.c.) was mixed with varying amounts of 0·05 M NaHS solution, and the total volume raised to 50 c. c. and the pH measured. The pH of the corresponding amounts of NaHS solutions was also

noted for comparison. The results are graphically represented in Fig.1, which shows that the pH of solutions goes on increasing with each addition of NaHS, until eight equivalents have been added, when the curve becomes almost constant. It also shows that some OH⁻ ions are released by the interaction of molybdate and sodium hydrosulphide
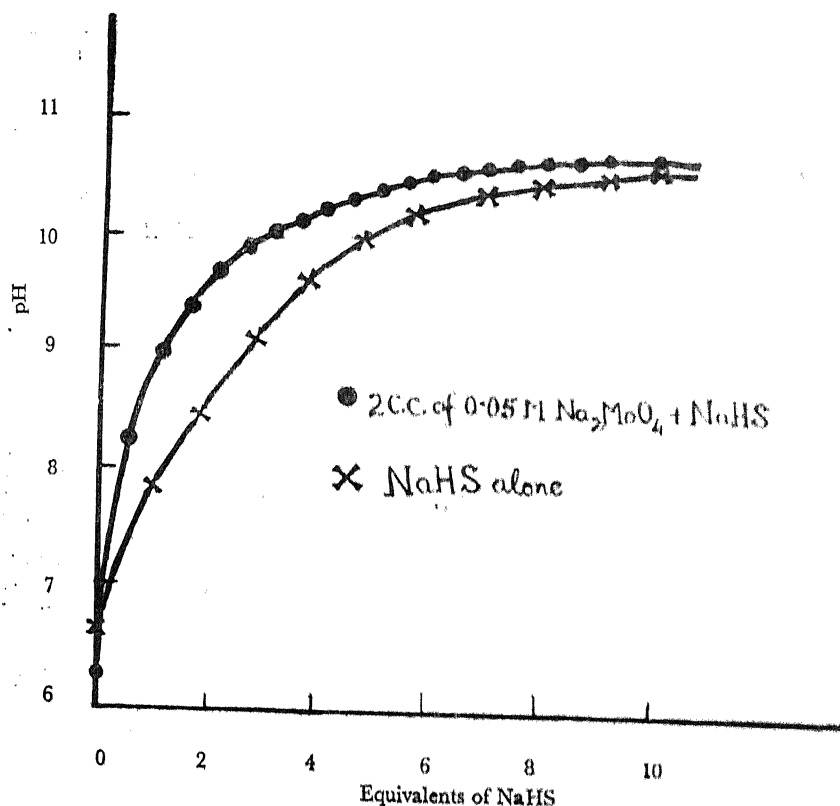

Equivalents of NaHS

Fig. 1.

(B) *Conductometric measurements :*

The conductivities of above solutions containing molybdenum and NaHS in various proportions were also measured at 33°C with an L. N. Kohlrausch slide wire with an audio-frequency oscillator. The conductance values of corresponding amounts of NaHS were also recorded. The results are given in fig. 2, in which the difference between the observed and the sum of the conductance of sodiummolybdate and corresponding amounts of NaHS have been plotted against the amounts of NaHS.

It shows that the slope of the curve changes at various stages, finally tending to be constant, where 8 mols. of NaHS to each of molybdenum have been added. It thus suggests the stepwise formation of a series of thioxy and thio molybdate compounds.

Potentiometric and Conductometric titrations of thioxy and thiomolybdates with HCl :

A standard 0·05 M sodium molybdate solution (2 c.c.) was mixed with a 0·05 M NaHS solution in various proportions (Mo : S=1:1 to 8). The thioxy and thio-

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molybdates so formed were acidified with varying amounts of 0·05 M HCl solution, and pH and conductance of the solutions measured. The total volume was kept
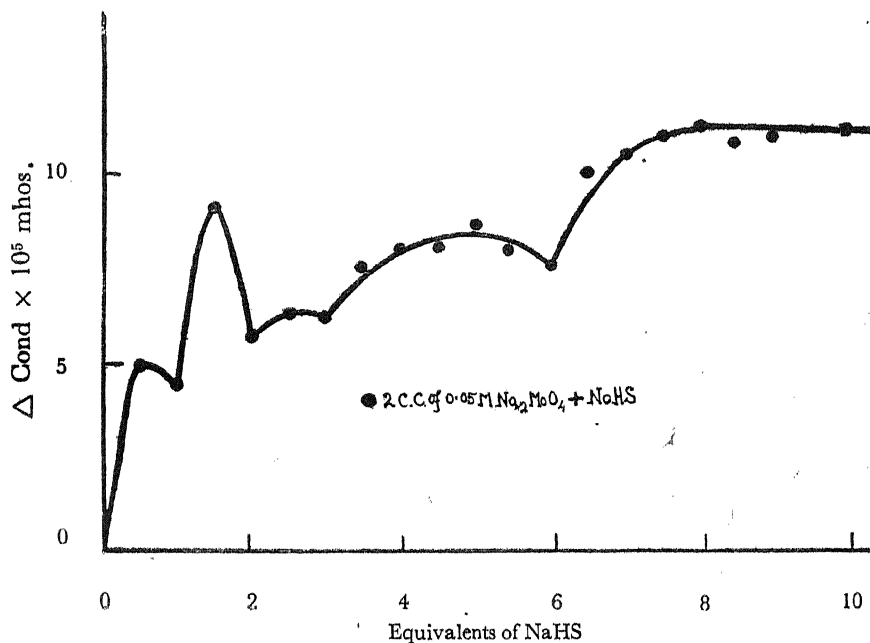
Fig. 2.

50 c.c. in each case. All the measurements of conductivity were done at $33\pm0\cdot1^{\circ}C$. The results are graphically represented in Figs.3 and 4.
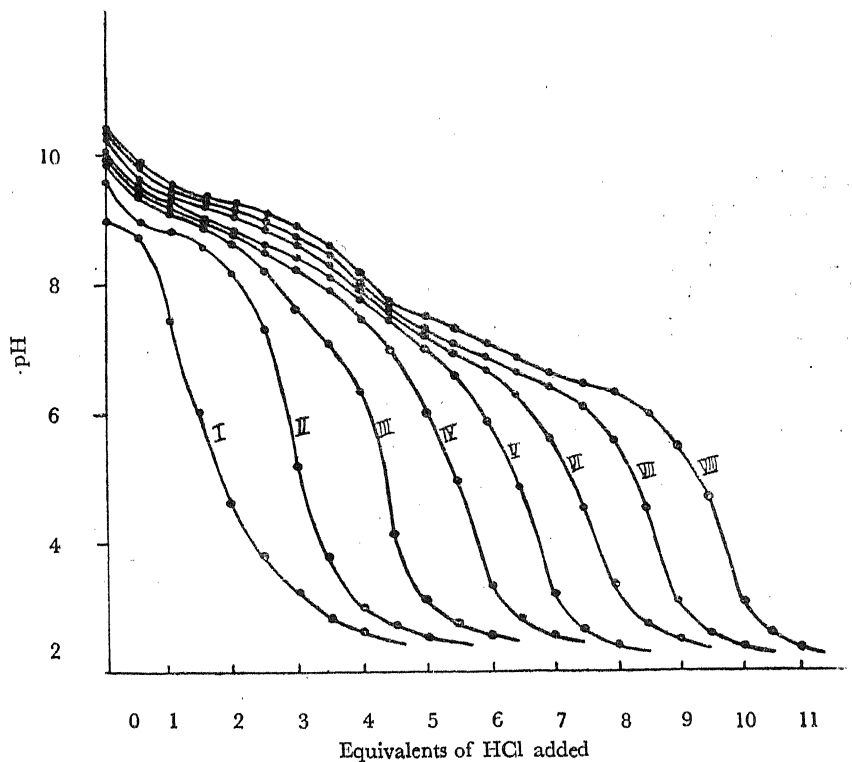
Fig. 3.

Fig. 3 shows the pH titration curves of thioxy and thio salts of molybdenum with hydrochloric acid. In general in all cases only one inflexion is well marked; the rest being so closely situated that nothing can be made out.
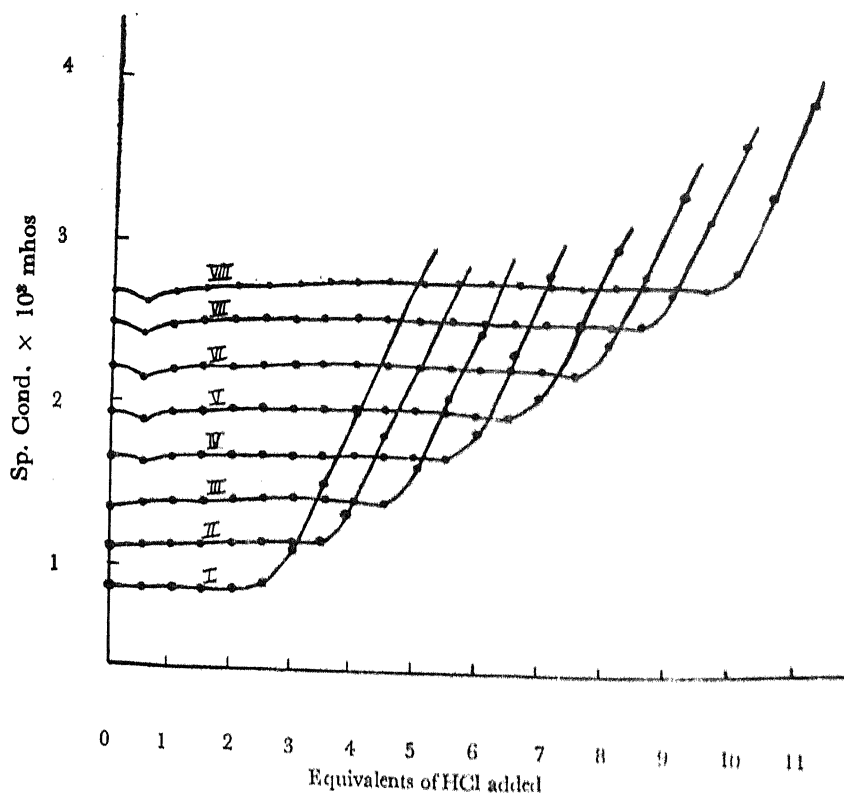
Fig. 4.

The conductometric titration curves (Fig.4) show that the conductance values in the initial stages remain almost constant in all cases. The curves rise very slowly until all the sodium present therein, is completely neutralised. On further addition of the acid the curves rise steadily. In curves from IV to VIII however a minimum may be said to appear where 1 c.c. of the acid has been added. Thus the nature of these curves remains essentially the same as obtained in the titration of thioxy and thioarsenates[a] i.e. the titration curve of weak base with a strong acid.

Colorimetric study of the decomposition of thiomolybdate with HCl :

On gradually adding hyprochloric acid to a solution of thiomolybdate, the colour of the solution changes from colourless to yellow-orange—orange-red, finally turning brown, and then molybdedum sulphide is precipitated. To study this colour change, a solution of thiomolydate (Mo : NaHS—1:8) was prepared and acidified with varying amounts of hydrochloric acid. 5 c. c. of 1% BaCl, solution was also added to coagulate any molybdenum sulphide. The total volume was kept at 50 c. c. in each case. Next day 10 c. c. of the solution was taken out, centrifuged

to clear off any suspension and diluted to 50 c. c. The intensity of the colour of the solutions was measured by a klett Summerson Photo-electric Colorimeter,
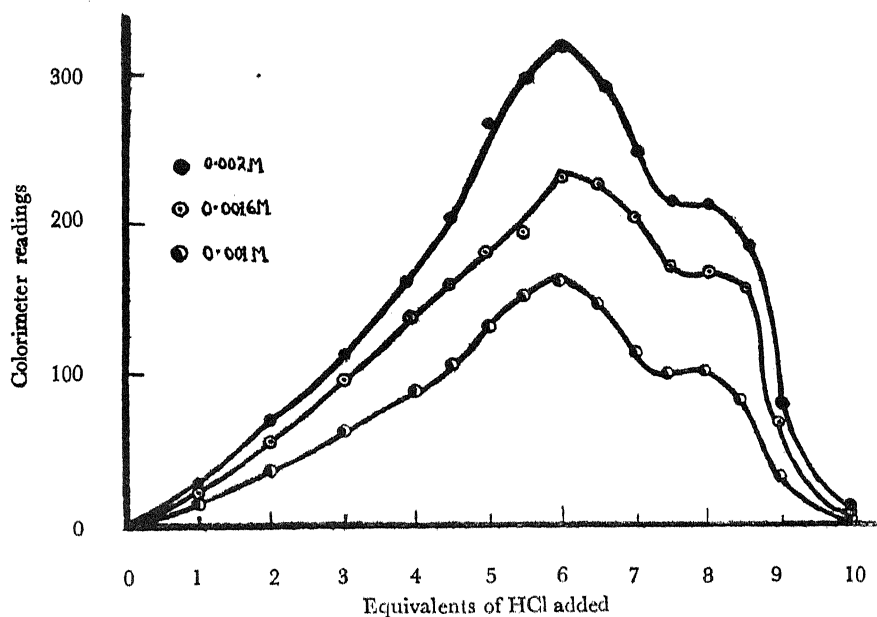
Fig. 5.
(Na. MoO₄ + 8 NaHS) Mixtures

using blue filter No. 42. The results are given in fig. 5, which shows that in each case two maxima are obtained, one at about 6 and the other at 8 equivalents of HCl, corresponding to four and two unneutralised sodium atoms in the solution. It thus indicates that thiomolydate forms two coloured thioanions $(H_6MoS_8)^{4-}$ and $(H_8MoS_8)^{2-}$ having yellow and orang-red colour respectively, before molybdenum sulphide is precipitated.

Thus the formation of thioxy and thiomolydates can be represented by the following set of ionic reversible reactions.

$$MoO_4^{2-} + HS^- \rightleftharpoons MoSO_3^{2-} + OH^-$$

$$MoSO_3^{2-} + HS^- \rightleftharpoons MoS_2O_2 + OH^-$$

$$MoS_2O_2^{2-} + HS^- \rightleftharpoons MoS_3O^{2-} + OH^-$$

$$MoS_3O^{2-} + HS^- \rightleftharpoons MoS_4^{2-} + OH^-$$

$$MoS_4^{2-} + 2HS^- \rightleftharpoons H_2MoS_6^{4-}$$

$$H_2MoS_6^{4-} + 2HS^- \rightleftharpoons H_4MoS_8^{6-}$$
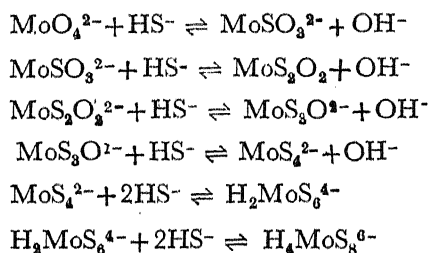
It is to be noted that in the first four steps OH⁻ ions are released at every stage of the reactions, i.e. with increasing acidity the formation of thiomolybdates is enhanced. But very few OH⁻ ions appear to exist in the free state in their solutions, so that the conductometric titration curves (fig. 4) do not show any well-marked drop in the initial stages. It is because of the reversibility of the reactions, so that the reaction proceeds to completion only when the OH⁻ ions are taken away from the system by adding acids. With gradual addition of acids it forms two coloured

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thioanions $H_6MoS_6{}^{4-}$ (yellow) and $H_8MoS_8{}^{2-}$ (orange-red) before molybdenum sulphide is precipitated. With further increase in hydrogen ion concentration, the dissociation of thiomolybdic acid is further suppressed, finally giving undissociated thiomolybdic acid molecules, which being unstable decompose immediately to give a precipitate of molybdenum sulphide and H_2S is liberated.

$$H_{10}MoS_8 = MoS_3 + 5H_2S,$$

It is further of interest to note that molybdenum is capable of forming a series of thiomolybdates having four, six and eight atoms of sulphur in their molecules. It is quite natural because molybdenum is well known to form compounds with coordination numbers 4, 6, and 8, and can expand its shell to accomodate as many as 16 shared electrons $i.e.$, its maximum covalency can be raised to eight. A theoretical explanation of this phenomenon can be had by considering the electronic structures of molybdenum and its compounds.

	K	L	M	N				O	
					s,	p	d	s	p
Mo (42)	2,	8,	18,	2,	6	⊙ ⊙ ⊙ ⊙ ⊙		(·)	
Mo (VI)	2,	8,	18,	2,	6,	O O O O O		( )	

Thus the lowest orbitals available for a Mo (VI) compound for co-ordination numbers 4, 6, and 8 will be as follows :

Co-ordination No.	Available orbitals	Configuration.	Structure
4,	$4d^35s$	d^3s	Tetrahedral[3]
	or $4d5sp^2$	dsp^2	Planar
6,	$4d^25sp^3$	d^2sp^3	Octahedral
8,	$4d^45sp^3$	d^4sp^3	Dodecahedron[4]

It may be seen that out of these four six and eight coordination compounds of molybdenum, a compound having maximum number of filled d orbitals can be had only when its co-ordination number is eight.

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STABILITY OF LYOPHOBIC SOLS

PART I. INFLUENCE OF THE NON - ELECTROLYTES, ACETONE AND ETHYL ALCOHOL

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ABSTRACT

Negatively charged MnO_2 sol of different average particle sizes was prepared and the cocgulation with potasium nitrate was studied in presence of different non electrolytes. It has been observed that ethyl alcohol and acetone sensitize the sol and the sensitization is in the order: acetone > ethyl alcohol. The degree of sensitization increased with the fineness of the dispersed particles and with the increasing concentration of added non electrolytes. It has been concluded that in the presence of ethyl alcohol and acetone, the adhesive tendency of the surface of dispersed particles increases, which enhances the frequency of collisions resulting in sensitization.

INTRODUCTION

Kruyt and Duyn[5] noted that isoamyl alcohol sensitized As_2S_3 sol towards mono-and trivalent coagulating ions but stabilised it towards divalent ones. Janeck and Jirgenson[4] noted that small amounts of alcohol sensitized As_2S_3 sol, while higher concentration stabilised it. Chatterji and Tewari,[2] reported that ethyl alcohol sensitized hydrous ferric oxide sol for K_2SO_4 and As_2S_3 sol for $BaCl_2$. We have studied here the effect of ethyl alcohol and acetone on the negatively charged MnO_2 sol for KNO_3 as the coagulating electrolyte. It was noted that sensitization is remarkably affected by the time of observation. We have, therefore, determined the coagulation values for infinite time in order to eliminate the time factor in the process of coagulation. Moreover, the surface of the dispersed material is also important and hence the effect of particle size has also been studied.

EXPERIMENTAL

Negatively charged MnO_2 sol was prepared by treating 0·1M $KMnO_4$ with a dilute solution of H_2O_2 so that a slight excess of permanganate was left over. The sol was purified by dialysing it for about a week in a cellophane bag. It was centrifuged in a Sharple's super-centrifuge at three speeds 6,000 r. p. m., 14,000 r. p. m. and 22,000 r. p.m., to have three samples A, B and C respectively with, different average sized particles. The content of MnO_2/lit was made the same in all samples (0·6667 gms of MnO_2/lit) by dilution whenever necessary.

2 ml of the sol was taken in one set of test tubes. Different amounts of coagulating electrolyte made upto 13 ml with distilled water were taken in another set and kept in a precision thermostat at 35·00 ± 0·05°C, till they attained the temperature of the bath. The contents were mixed and left immersed in the thermostat undisturbed. The time of complete coagulation was noted at the point of visual separation of clear liquid at the upper surface of the test tube. The coagulation value for infinite time has been obtained by extrapolation.

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In the following table we are reproducing some of our results on the sensitization of sol A by ethyl alcohol and acetone towards its coagulation by different quantities of 0·02 N KNO₃ solution.

TABLE 1

0·02 NKNO₃ ml.	Time of coagulation $t \times 10^{-3}$ seconds.		
	No non-electrolyte	3·0% Ethyl alcohol	3·0% acetone.
8·0	2·000	1·310	0·480
7·0	2·340	1·520	0·600
6·0	2·580	2·010	0·910
5·0	3·260	2·500	1·150
4·0	4·560	3·480	1·560
3·0	5·495	4·115	2·370
2·0	6·250	4·900	3·830
1·0	12·300	10·000	5·780

In Tables II-IV, the values of (time of coagulation)⁻¹ are given for different amounts of coagulating electrolyte.

TABLE 2

0·02N NKO₃ ml.	$1/t \times 10^4$ Seconds		
	Sol A	Sol B	Sol C
8·0	5·000	4·717	4·587
7·0	4·274	4·065	3·876
6·0	3·876	3·846	3·676
5·0	3·067	2·959	2·857
4·0	2·193	2·137	2·083
3·0	1·819	1·783	1·745
2·0	1·600	1·570	1·541
1·0	0·813	0·802	0·804

TABLE 3

0·02N KNO₃ ml	1/t × 10⁴ seconds								
	Concentration of Ethyl Alcohol								
	1·0%			2·0%			3·0%		
	Sol A	Sol B	Sol C	Sol A	Sol B	Sol C	Sol A	Sol B	Sol C
8·0	6·993	6·410	6·173	7·299	6·711	6·452	7·634	6·944	6·667
7·0	6·135	5·714	5·525	6·369	5·917	5·714	6·579	6·098	5·882
6·0	4·695	4·444	4·329	4·831	4·566	4·444	4·975	4·673	4·545
5·0	3·817	3·650	3·571	3·906	3·731	3·650	4·000	3·802	3·717
4·0	2·778	2·688	2·646	2·825	2·732	2·681	2·874	2·770	2·725
3·0	2·364	2·294	2·262	2·398	2·331	2·299	2·433	2·358	2·326
2·0	1·992	1·946	1·923	2·016	1·969	1·942	2·041	1·988	1·965
1·0	0·988	0·976	0·970	0·994	0·982	0·977	1·002	0·990	0·934

TABLE 4

0·02N KNO₃ ml	1/t × 10⁴ seconds								
	Concentration of Acetone								
	1·0%			2·0%			3·0%		
	Sol A	Sol B	Sol C	Sol A	Sol B	Sol C	Sol A	Sol B	Sol C
8·0	17·240	14·290	13·160	18·870	15·380	14·080	20·830	16·670	15·150
7·0	14·290	12·200	11·360	15·380	12·990	12·050	16·670	13·890	12·820
6·0	9·901	6·850	8·403	10·420	9·259	8·772	10·990	9·709	9·174
5·0	8·000	7·299	6·993	8·333	7·576	7·246	8·696	7·874	7·519
4·0	5·988	5·587	5·405	6·211	5·780	5·587	6·410	5·952	5·747
3·0	4·049	3·861	3·774	4·132	3·937	3·846	4·219	4·016	3·922
2·0	2·551	2·475	2·439	2·577	2·500	2·463	2·611	2·532	2·494
1·0	1·701	1·667	1·650	1·715	1·681	1·664	1·730	1·695	1·678

a, the coagulation value for infinite time may be taken as a measure of the stability of the sol. In the following table we present the values of *a*.

TABLE 5

Non-electrolyte	*a* ml of 0·02N KNO₃		
	Sol A	Sol B	Sol C
No non-electrolyte	0·50	0·55	0·60
3·0% Ethyl alcohol	0·40	0·40	0·45
3·0% Acetone	0·30	0·35	0·35

Bhattacharya *et al*[1] gave an empirical equation

$$\frac{1}{c-a} = \frac{n}{m}\,t + \frac{1}{m} \qquad \ldots\ldots(i)$$

Eq. (*i*) has been found to agree well with the experimental data. The values of $1/(c-a)$ and *t* are given in the following table.

TABLE 6

Sol A + 0% non-electrolyte		Sol A + 3% Ethyl alcohol		Sol A + 3% Acetone	
$1/(c-a) \times 10^{-1}$ eq/lit	$E \times 10^{-2}$ seconds	$1/(c-a) \times 10^{-1}$ eq./lit.	$t \times 10^{-2}$ seconds	$1/(c-a) \times 10^{-1}$ eq./lit.	$t \times 10^{-2}$ seconds.
10·26	20·00	10·12	13·10	10·00	4·80
11·83	23·40	11·66	15·20	11·48	6·00
13·99	25·80	13·74	20·10	13·50	9·10
17·09	32·60	16·72	25·00	16·37	11·50
21·98	45·60	21·37	34·80	20·79	15·60
30·77	54·95	29·59	41·15	28·49	23·70

The scope of the straight line (fig. 1) obtained by plotting $1/(c-a)$ against t gives the value n/m and the intercept on $1/(c-a)$ axis gives $1/m$. The values obtained for sol A are recorded below :—

TABLE 7

Non Eletrolyte		$1/m$	m	n/m	n
No non-electrolyte	...	25·0	0·040	0·0425	0·0017
3·0% Ethyl alcohol	...	30·0	0·033	0·0550	0·0018
3·0 % Acetone	...	50·0	0·020	0·0950	0·0019
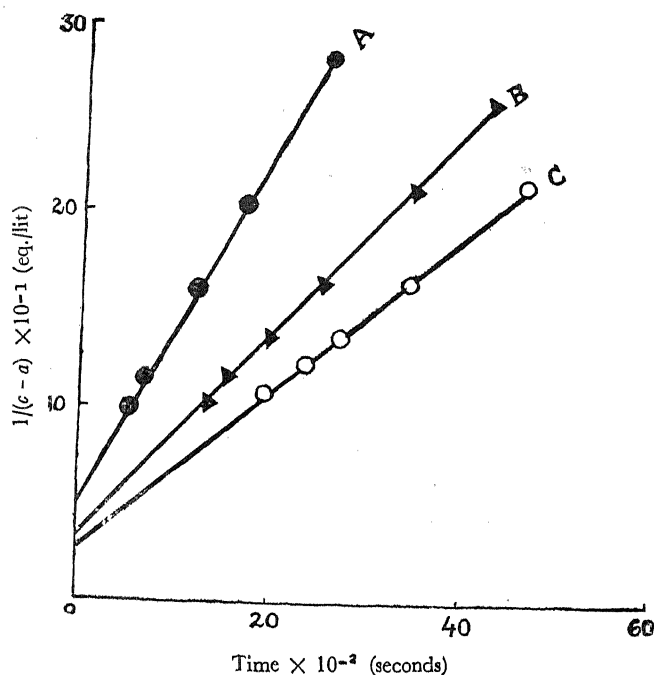
Figure 1.

Curve A : Potassium nitrate + 3·0 % Acetone ;
Curve B : Potassium nitrase + 3·0 % Ethyl Alcohol;
Curve C: Potassium nitrate + No non-electrolyte.

RESULTS AND DISCUSSION

It is clear from Table 1 that the extent of sensitization is more remarkable when the time of coagulation is small than that observed when the time of coagulation is large as brought about by smaller amount of coagulating electrolyte.

A pursual of table 5 reveals that the sol with average finer particles is more stable than with average coarser ones. The order of stability is sol C > sol B > sol A.

Both acetone and ethyl alcohol sensitize negatively charged MnO_2 sol and the order of sensitizing power is acetone > ethyl alcohol. Further the degree of sensitization is more pronounced with the sol containing average finer particles than with the coarser ones. The sensitization, however, increases with the increase of added non electrolyte from 1.0 % to 3.0 %.

It will be seen from Table 7 that m of equation (i) decrease while n increases in presence of either ethyl alcohol or acetone. Ghosh et al[3] have shown that n may be taken as equal to $1/T$ where T is the time taken for coagulation at a sufficiently high concentration of added electrolyte. According to Smoluchowski :

$$T = 1/(8 \pi D r n_0).$$

In the presence of small concentration of non electrolyte D and n_0 remain almost unaltered. As n increases in presence of non-electrolyte, we infer that T decreases and the decrease of T is possible if the effective distance of attraction r increases. We conclude that in the presence of ethyl alcohol and acetone the adhesive tendency of the surface of dispersed particles increases which enhances the frequency of collisions resulting in sensitization.

ACKNOWLEDGEMENT

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STABILITY OF LYOPHOBIC SOLS

PART II. INFLUENCE OF THE NON-ELECTROLYTES, GLUCOSE, UREA AND GELATIN

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[Received on 22nd August, 1960]

ABSTRACT

The coagulation of negatively charged MnO$_2$ sol of different average particle sizes by KNO$_3$ has been studied in the presence of different non-electrolytes *viz.*, glucose, urea and gelatin. It has been observed that these stabilize the sol. The order of stabilizing power is gelatin $>$ urea $>$ glucose. The degree of stabilization increases with the fineness of dispersed particles and with the increasing concentration of added non-electrolyte. It has been concluded that the adhesive tendency of the surface of dispersed particles decreases in the presence of said non-electrolytes, resulting in stabilization.

INTRODUCTION

Keesom[4] observed that urea and glycol stabilise As$_2$S$_3$ sol towards electrolytes. Mukerjee[5] found decreasing cataphoretic speeds of colloid particles of As$_2$S$_3$ sol in presence of sugar. Jirgenson[3] found stabilisation by urea, acetamide and formamide on different sols. Sen[6] observed stabilisation of MnO$_2$ sol by sugar. Here we have studied the influence of urea, glucose and gelatin on the stability of an MnO$_2$ sol.

EXPERIMENTAL

Three samples of negatively charged MnO$_2$ sol were obtained which contained different average sized particles. The samples A, B and C contained 0·666 gm. MnO$_2$/lit. the time of complete coagulation was noted at 35·00 $\pm$ 0·05°C for KNO$_3$ as coagulating electrolyte with and without the addition of glucose, urea and gelatin. The experimental details are given in Part I of the series.[7]

In the following table we are reproducing a some of our results on the stabilisation of sol A by glucose, urea and gelatin towards its coagulation by KNO$_3$.

TABLE 1

0·02N KNO$_3$ ml.	Time of coagulation $t \times 10^{-3}$ seconds			
	No non-electrolyte	3·0 % Glucose	3·0 % Urea	0·03 % Gelatin
8·0	2·000	2·460	3·060	5·879
7·0	2·340	2·580	3·340	7·018
6·0	2·580	2·970	4·210	9·615
5·0	3·260	3·630	5·400	16·610
4·0	4·560	5·120	7·310	22·730

In Tables 2—5 the values of 1/(time of coagulation) are given for different amounts of coagulating electrolyte.

<div align="center">TABLE 2</div>

0·02N KNO₃ ml.	1/t × 10⁴ seconds		
	Sol A	Sol B	Sol C
8·0	5·000	4·717	4·587
7·0	4·274	4·065	3·876
6·0	3·876	3·846	3·676
5·0	3·067	2·959	2·857
4·0	2·193	2·137	2·083
3·0	1·819	1·783	1·745
2·0	1·600	1·570	1·541
1·0	0·813	0·802	0·804

<div align="center">TABLE 3</div>

0·02N KNO₃ ml.	1/t × 10⁴ seconds								
	Concentration of Glucose								
	1·0 %			2·0 %			3·0 %		
	Sol A	Sol B	Sol C	Sol A	Sol B	Sol C	Sol A	Sol B	Sol C
8·0	4·802	4·388	3·770	4·761	4·346	3·733	4·650	4·230	3·612
7·0	4·001	3·562	3·356	3·960	3·521	3·311	3·876	3·411	3·201
6·0	3·452	3·011	2·880	3·412	2·970	2·822	3·376	2·880	2·712
5·0	2·842	2·421	2·156	2·801	2·366	2·114	2·755	2·256	2·005
4·0	2·026	1·700	1·506	1·988	1·663	1·466	1·953	1·535	1·346
3·0	1·331	1·019	0·849	1·263	0·972	0·802	1·161	0·861	0·700
2·0	0·710	0·568	0·466	0·690	0·522	0·422	0·580	0·412	0·310

TABLE 4

0·02N KNO₃ ml.	1/t × 10⁴ second								
	Concentration of Urea								
	1·0 %			2·0 %			3·0 %		
	Sol A	Sol B	Sol C	Sol A	Sol B	Sol C	Sol A	Sol B	Sol C
8·0	3·378	3·356	3·333	3·322	3·300	3·274	3·268	3·240	2·866
7·0	3·077	3·058	3·040	3·030	3·012	2·994	2·994	2·851	2·698
6·0	2·433	2·415	2·404	2·404	2·387	2·370	2·375	2·156	2·002
5·0	1·887	1·876	1·869	1·873	1·866	1·859	1·852	1·610	1·495
4·0	1·389	1·383	1·379	1·379	1·376	1·372	1·368	1·188	1·026
3·0	0·770	0·701	0·612	0·760	0·652	0·581	0·750	0·631	0·541
2·0	0·361	0·300	0·291	0·352	0·281	0·260	0·301	0·255	0·235

TABLE 5

0·02N KNO₃ ml.	1/t × 10⁴								
	Concentration of Gelatin								
	0·01 %			0·02 %			0·03 %		
	Sol A	Sol B	Sol C	Sol A	Sol B	Sol C	Sol A	Sol B	Sol C
8·0	1·901	1·832	1·601	1·812	1·660	1·466	1·701	1·504	1·320
7·0	1·642	1·471	1·255	1·560	1·336	1·140	1·425	1·200	1·004
6·0	1·206	1·043	0·894	1·142	0·961	0·882	1·004	0·775	0·625
5·0	0·941	0·722	0·502	0·750	0·534	0·461	0·602	0·456	0·351
4·0	0·550	0·360	0·286	0·450	0·266	0·220	0·440	0·250	0·204
3·0	0·301	...	...	0·251	---	...	0·210	...	...

The coagulation value for infinite time may be taken as a measure of the stability of the sol. In the following table we present the values of a (Coagulation value for infinite time).

TABLE 6

Non-electrolyte		a ml. of 0·02N KNO_3		
		Sol A	Sol B	Sol C
No non-electrolyte	...	0·50	0·55	0·60
3·0 % Glucose	...	0·70	0·80	0·90
3·0 % Urea	...	1·00	1·10	1·30
0·03 % Gelatin	...	2·00	2·20	2·40

Bhattacharya et al[1] gave an empirical equation,

$$\frac{1}{c-a} = \frac{n}{m} t + \frac{1}{m} \qquad \cdots (i)$$

Eq. (i) has been found to agree well with the experimental data. The values of $1/(c-a)$ and t for sol A are given in the following table.

TABLE 7

No non-electrolyte		3·0 % Glucose		3·0 % Urea		0·03 % Gelatin	
$1/(c-a)$ $\times 10^{-1}$ eq./lit	$t \times 10^{-2}$ seconds	$1/(c-a)$ $\times 10^{-1}$ eq./lit	$t \times 10^{-2}$ seconds	$1/(c-a)$ $\times 10^{-1}$ eq./lit	$t \times 10^{-2}$ seconds	$1/(c-a)$ $\times 10^{-1}$ eq./lit	$t \times 10^{-2}$ seconds
10·26	20·00	10·54	24·60	10·99	30·60	12·82	58·80
11·83	23·40	12·21	25·80	12·82	33·40	13·99	65·10
13·99	25·80	14·51	29·70	15·38	42·10	15·38	70·20
17·09	32·60	17·89	36·30	19·23	54·00	...	...
21·98	45·60	23·31	51·20	25·64	73·10	...	...

The slope of the straight line obtained by plotting $1/(c-a)$ against t (fig. 1) gives the value n/m and the intercept on $1/(c-a)$ axis gives $1/m$. The values obtained for sol A are recorded below.

TABLE 8

Non-electrolyte		1/m	m	n/m	n
No non-electrolyte	...	25·0	0·0400	0·0425	0·001700
3·0 % Glucose	...	24·5	0·04082	0·04125	0·001684
3·0 % Urea	...	20·0	0·0500	0·03125	0·0015625
0·03 % Gelatin	..	15·0	0·06667	0·0200	0·0013334
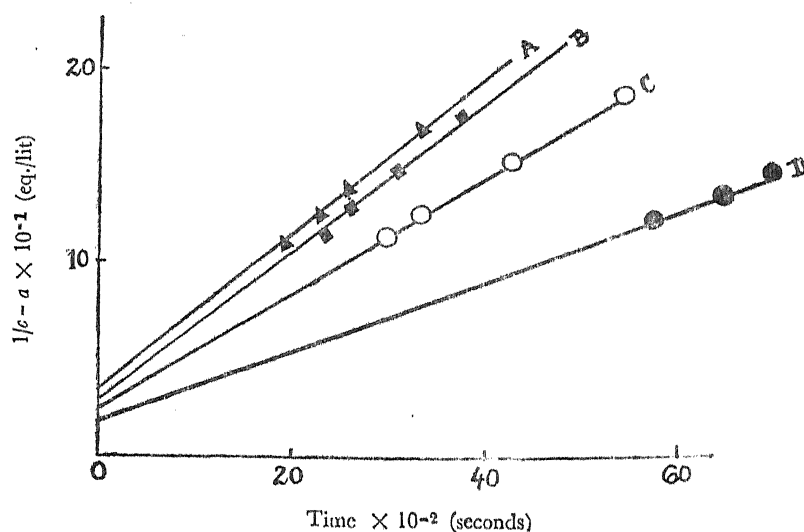
Figure 1.

Curve A : Potassium nitrate + no non-electrolyte ;
Curve B : Potassium nitrate + 3·0% glucose ;
Curve C : Potassium nitrate + 3·0% urea ;
Curve D : Potassium nitrate + 0·03% gelatin.

RESULTS AND DISCUSSION

It is clear from table I that the extent of stabilization is more remarkable when the time of coagulation is large as brought about by smaller amounts of coagulating electrolyte.

The order of the stability of three samples is Sol C > Sol B > Sol A. Glucose, urea and gelatin stabilize MnO_2 sol and the order of stabilizing power is gelatin > urea > glucose. The degree of stabilization increases with the fineness of dispersed particles and with the increasing concentration of added non electrolyte.

It will be seen from table 7 that m of eq. (i) increases, while n decreases in presence of glucose, urea and gelatin. According to Smoluchowski $T = 1/8 \pi D r n_0$,

[197]

Ghosh et al^2 have shown that n may be taken as equal to $1/T$. In the presence of small concentrations of added non-electrolyte D, and n_0 remain almost unaltered. A decrease in the value of n or an increase in the value of T is attributed to a decrease in the value of r (effective distance of attraction). We, therefore, conclude that in the presence of glucose, urea and gelatin the adhesive tendency of the surface of dispersed particles decreases which lowers the frequency of collision and results in stabilization.

ACKNOWLEDGEMENT

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ABSORPTIOMETRIC INVESTIGATION OF THE REACTION BETWEEN HEXAVALENT CHROMIUM AND OXALATE IN PRESENCE OF MANGANOUS SULPHATE

By

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ABSTRACT

The reaction between hexavalent chromium and oxalate has been studied by using the catalyst, manganous sulphate. Proper control of the acidity of the reaction mixture gives rise to a red coloured compound in the system which has been detected as the mangani-oxalate complex where manganese is trivalent. SP 500 Unicam spectrophotometer is used for detecting the absorption behaviour of the complex. Standard volumetric estimation and the colorimetric determination are carried out simultaneously for quantitative estimation of the different oxidants present. A general theory has been put forward to explain the mechanism of the reaction.

INTRODUCTION

The oxidation of oxalate by hexavalent chromium in the form of chromic acid has been studied by various workers [1-4] and a thorough study of the reaction has already been made by us[5] regarding kinetic constants of the system. The reaction between hexavalent chromium and oxalate is found to be catalysed by bivalent manganese. A closer study of the system reveals that the characteristics of the induced reaction is marked in the above case where the reaction between hexavalent chromium and manganous ion is found to induce the oxidation of oxalate. It is also hinted in our previous communication that the path of the chemical reaction is entirely changed by the introduction of the bivalent manganese in the reaction mixture. The detailed mechanism involved therein has been discussed in the present paper.

In the course of the study of the influence of bivalent manganese on the reaction between oxalate and dichromate it is observed that the reaction mixture develops a purple colour which after becoming much intense, gradually fades away. This observation clearly indicates the formation of some unstable intermediate compound during the course of the reaction and identification of the above compound is made by the spectrophotometric measurements.

Trivalent manganese in the form of the cation or coordinate complex radical is reported in the literature.[6] The species are said to possess a purple colour in solution. Launer,[7] Taube[8], Cabello,[8] Iber and Devidson,[10] and many other workers investigated the physico-chemical properties of the purple manganioxalate complex. In all the above cases the less familiar trivalent state of manganese is

obtained by reducing some highervalent salt as manganese dioxide or potassium permanganate. But in our present investigation the trivalent manganese is prepared without using any highervalent manganese salt. The purple coloured intermediate, generated during the course of the reaction between hexavalent chromium and oxalate in presence of manganous sulphate is suspected to be a complex of the trivalent manganese which has been verified spectrophotometrically.

Spectrophotometric Identification of the Intermediate Complex :

Reagents are prepared out of A. R. grade chemicals and standardised by the usual quantitative methods. Equal amounts of oxalic acid and potassium oxalate of the same strength are mixed for obtaining the potassium acid oxalate which is found to be an ideal source of the oxalate radical.

Known samples of potassium manganioxalate is produced by the reaction between manganese dioxide and potassium acid oxalate. The absorption maxima for the complex thus prepared, is obtained by using a Unicam SP 500 Spectrophotometer.

Difficulties arise in the spectrophotometric study due to the continuous and fast decomposition of the potassium mangani-oxalate. The absorption is essentially to be examined for different wave lengths for a coloured species having a constant strength for determining the maxima. Because it is not possible to perform the experiment with a single sample of the unstable complex, to a fixed amount of freshly precipitated manganese dioxide a measured volume of potassium acid oxalate is added to obtain the clear purple coloured mangani-oxalate solution after a certain time lapse. Number of identical samples thus produced are used at different wavelengths of the spectrophotometer at the same time interval to complete the whole absorption curve. (Curve A, fig. 1).

On locating the absorption maxima for the mangani-oxalate complex prepared from manganese dioxide, similar investigation is made for the purple coloured intermediate compound formed during the course of the reaction between potassium acid oxalate and dichromate in the presence of bivalent manganese. The absorption curve obtained in this case (curve B, fig. 1) shows the maxima (point Y) at the same wavelength as in the first case. The differences in the total percentage of absorption is of course, due to the difference in strengths of the manganioxalate formed in two cases. Nevertheless, the coloured compounds are characterised by the absorption maxima and when they are identical (457 mμ) for both the species, it is established that the purple coloured compound generated during the course of the reaction between potassium acid oxalate and dichromate in presence of bivalent manganese is undoubtedly the complex of mangani-oxalate where manganese is having a valency of three.

Colorimetric Investigation of the Trivalent Manganese Complex during the Progress of the Reaction :

The reaction between oxalic acid and chromic acid is one which is found to be largely investigated, (loc. cit.) Even then it is surprising that the early workers overlooked the formation of intermediate manganic complex in the system, where bivalent manganese was used as catalyst. The fact has been discussed in our previous communication[5] and there it has been also indicated, how

it is possible to visualise the complex. Unfortunately the usual volumetric estimation for the total oxidant present at any instance of the reaction is not able to point out separately the amount of trivalent manganese. For this reason the colorimetric estimations are carried out which quantitatively indicates the amount of complex generated at any time of the reaction.
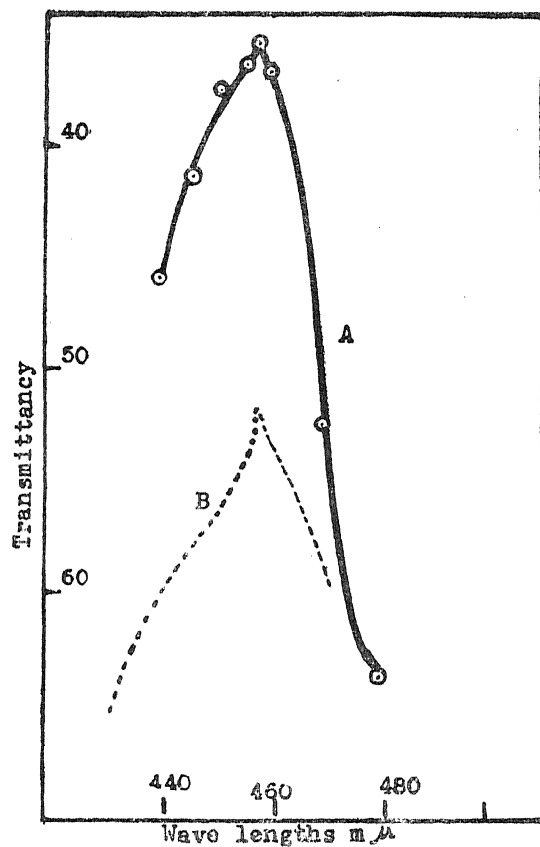
Fig. 1. Showing concurrent peaks of absorption for the trivalent manganese prepared from potassium permanganate and potassium dichromate as the oxidant.

Complete reaction rate has been followed by the colorimetric estimation of trivalent manganese along with the iodometric estimation of the total oxidant present.

The reaction mixtures are placed in a precision thermostat (Townson and Mercer Ltd.) kept in a temperature controlled room so that the variation of the temperature between the bath and the room is between $0 \cdot 1^{\circ}C$. Two Jena bottles wrapped with black cloth to avoid photochemical effect, if any, one containing the oxalate and the dichromate and manganous sulphate, are first kept in the bath. When temperature is attained they are mixed together and time is noted. At different intervals of time 5 c.c. of the reaction mixture is pipetted out and are introduced to Klett's tube for noting the absorption in the Klett Summerson's photoelectric colorimeter. Standard filter no. 69 (transmission $660\text{-}740m\mu$) is

used when the complete transmission take place for the colours of hexavalent chromium and trivalent chromium and the colorimeter reads only for the purple coloured mangani-oxalate complex. The colorimeter is previously standardised for this complex prepared from manganese dioxide and oxalate.

As soon as the colorimetric readings are noted the whole solution is poured to an acidified potassium iodide solution. It should be mentioned here that hardly fifteen seconds are needed for noting the colorimetric readings and the time is noted at the moment when the solution is transferred from the tube to the iodide solution.

From the absorption data the manganese present in the trivalent form is calculated and from the amount of total oxidant, the value of the trivalent manganese is subtracted to give the value for only highervalent chromium. This highervalent chromium has been calculated as hexavalent in terms of chromium trioxide. The amount of oxalate lost is equal to the amount of oxidant used up and so the amount of carbon dioxide produced has been calculated from this data. In the
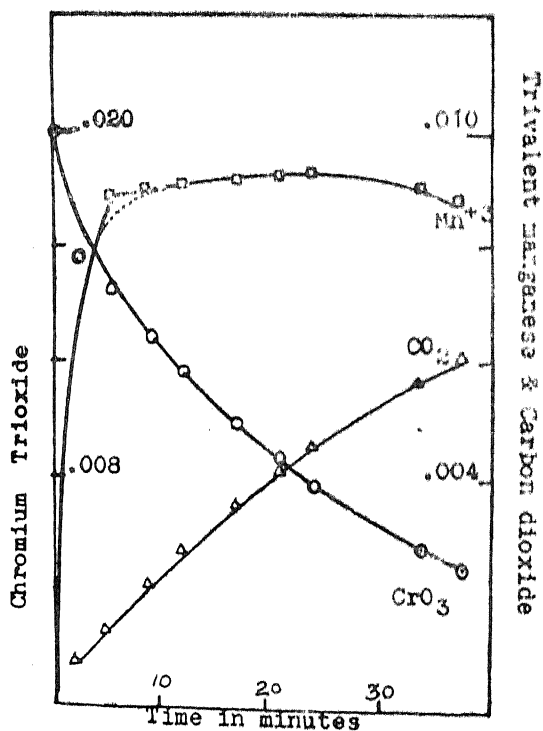
Fig. 2. Progress of the reaction at a sulphuric acid medium of strength 0·05 N.

following tables columns 5, 6 and 7 represents trivalent manganese, chromium trioxide, and carbon dioxide respectively. These values for different sets are plotted in fig 2-4. From these graphs it will be seen that with the progress of the reaction

the amount of carbon dioxide continuously increases, the amount of hexavalent chromium decreases but the trivalent manganese passes through a maximum.
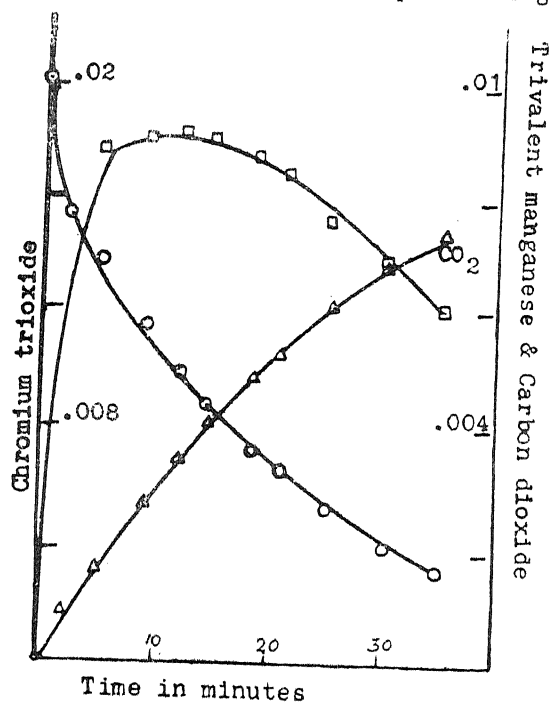
Fig. 3. Progress of the reaction at a sulphuric acid medium of strength 0·1 N.
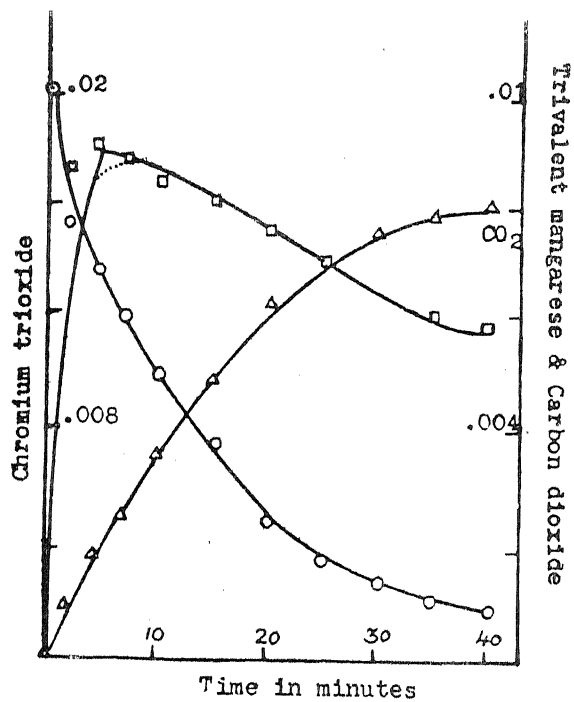
Fig. 4. Progress of the reaction at a sulphuric acid medium of strength 0·15 N.

Ratio between oxalic acid and potassium oxalate ... 1 : 1
Strength of total oxalate ... 0·05 M
Strength of potassium dichromate ... 0·01 M
Strength of manganous sulphate ... 0·008 M
Temperature of the bath ... 30°C
Factor of the colorimeter ... 0·000136

TABLE 1

Concentration of the sulphuric acid ... 0·05 N

1	2	3	4	5	6	7
0·0	0·0	12·00	6 00	0·00	20·00	0·00
2·0	64·0	11·12	5·56	8·70	15·64	0·73
4·5	65·5	10·48	5·24	8·91	14·50	1·27
9·0	66·0	9·48	4·74	8·98	12·80	2·10
12·0	66·5	8·76	4·38	9·04	11·58	2·70
17·0	67·0	7·76	3·88	9·11	9·90	3·53
21·0	67·5	7·04	3·52	9·18	8·68	4·13
24·0	68·0	6·56	3·28	9·25	7·86	4·53
33·5	66·5	5·16	2·58	9·04	5·58	5·70
37·0	65·0	4·68	2·34	8·84	4·86	6·10
45·0	62·0	3·72	1·86	8·43	3·40	6·90

TABLE II

Concentration of the sulphuric acid ... 0·10 N

1	2	3	4	5	6	7
0·0	0·0	12·00	6·00	0·00	20·00	0·00
2·0	64·0	10·92	5·46	8·70	15·30	0·90
4·5	67·0	9·84	4·92	9·11	13·69	1·80
7·0	65·0	9·00	4·50	8·84	12·05	2·50
10·0	62·0	7·64	3·82	8·43	9·92	3·60
15·0	59·5	6·12	3·06	8·09	7·50	4·90
20·0	56·0	4·40	2·20	7·62	4·79	6·30
25·0	52·0	3·48	1·74	7·07	3·44	7·10

TABLE III

Comcentration of the sulphuric acid = 0·15 N

1	2	3	4	5	6	7
0·0	0·0	12·00	6·00	0·00	20·00	0·00
2·0	64·0	10·92	5·46	8·70	15·30	0·90
4·5	67·0	9·84	4·92	9·11	13·69	1·80
7·0	65·0	9·00	4·50	8·84	12·05	2·50
10·0	62·0	7·64	3·82	8·43	9·92	3·60
15·0	59·5	6·12	3·06	8·09	7·50	4·90
20·0	56·0	4·40	2·20	7·62	4·78	6·30
25·0	52·0	3·48	1·74	7·07	3·44	7·10

Columns :

1. Time in minutes.

2. Colorimeter reading.

3. Sodium thiosulphate (N/40) used for 5c.c. of solution.

4. Total oxidant in normality × 1000.

5. Trivalent manganese in molarity × 1000.

6. Hexavalent chromium in molarity × 1000.

7. Carbon dioxide in molarity × 1000.

The nature of the curves plotted show distinct indication of the consecutive type of the reaction.[11] Such cases of the consecutive reactions are difficult to demonstrate due to the experimental complexities. Simultaneous quantitative estimation by colorimetric and volumetric methods in our present investigation reveals a way to study any type of consecutive reactions which involves some coloured species as the oxidising agent.

General Discussion of the Results

In oxidation-reduction processes where electron exchange occurs, normally the mechanism involves one electron change at a time.[12,13] Where the valency changes are more than one, it is reasonable to believe that the reaction passes through a number of intermediate stages. Hexavalent chromium, in its reduction to trivalent stage passes through intermediate pentavalent and tetravalent condition, i.e. three steps are involved in the reaction. The reaction between similarly charged ions is usually slow and so the reaction between bivalent oxalate and chromate will have negative entropy for the transitory state and will be very slow. In more acidic

solution, however the undissociated chromic acid is obtained because it is comparatively a weak acid and hence undissociated molecules of chromic acid is more reactive towards oxalate than the chromate anion. Needless to say that the reaction between oxalate and CrO_3^- is again likely to be very slow. In presence of large amounts of an acid, CrO_3^- may be converted to Cr^{+5} which is more favourable to react with a negatively charged oxalate producing chromium in the tetravalent stage. The mention of pentavalent and tetravalent chromium as Cr^{+5} and Cr^{+4} is not rare in literature.[14-16] We, may therefore conclude that the reaction between a chromate and oxalate in acid solution is guided by the following scheme :

$$CrO_4^{--} + 2 H^+ \quad = \quad H_2CrO_4$$

$$= \quad H_2O \quad + \quad CrO_3 \qquad (i)$$

$$CrO_3 \quad + \quad C_2O_4^{--} \quad = \quad CrO_3^- \quad + \quad C_2O_4^- \qquad (ii)$$

$$C_2O_4^- \quad + \quad CrO_3 \quad = \quad CrO_3^- \quad + \quad 2\,CO_2 \qquad (iii)$$

$$CrO_3^- \quad + \quad 6\,H^+ \quad = \quad Cr^{+5} \quad + \quad 3\,H_2O \qquad (iv)$$

$$Cr^{+5} \quad + \quad C_2O_4^{--} \quad = \quad Cr^{+4} \quad + \quad C_2O_4^- \qquad (v)$$

$$C_2O_4^- \quad + \quad Cr^{+5} \quad = \quad Cr^{+4} \quad + \quad 2\,CO_2 \qquad (vi)$$

$$Cr^{+4} \quad + \quad C_2O_4^{--} \quad = \quad Cr^{+3} \quad + \quad C_2O_4^- \qquad (vii)$$

$$Cr^{+4} \quad + \quad C_2O_4^- \quad = \quad Cr^{+3} \quad + \quad 2\,CO_2 \qquad (viii)$$
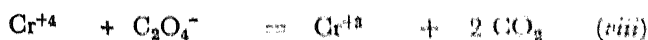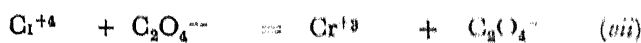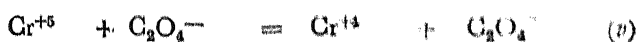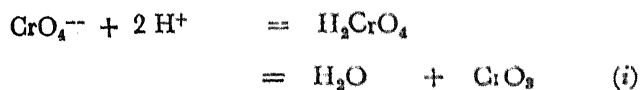
Steps (iii), (vi) and (viii) of the above equations are expected to be rapid and also the step (iv) in highly acid solutions may be considered to be instantaneous. Thus, in the reaction between hexavalent chromium and oxalate in acid medium any of the processes (ii), (v) and (vii) will be rate determining. If the velocities of these reactions are comparable, the overall chemical change will be of consecutive type, which usually shows induction period. But it will be seen from our results[5] and as well as from those of other workers[17] that this reaction has no induction period which confirms that only one of the reactions determine the speed. We have shown that the reaction is unimolecular with respect to hexavalent chromium but bimolecular with respect to oxalate.[5] So, it appears that the equation (v) determines the speed.

The above mechanisms clarify the part played by an acid in the reaction. It is clear that the neutral molecules of chromic acid or CrO_3 are necessary for the step (ii) and (iii) of the reaction. For further progress of the reaction highervalent positively charged chromium cation is necessary for the continuation of the reaction to an end.

It is now necessary to consider the results on the enhanced oxidation rate of oxalate by hexavalent chromium, in the presence of manganous sulphate. It is found that the decrease in the total oxidant i.e. the amount of oxalate oxidised is unimolecular with respect to hexavalent chromium, but with the increasing concentration of manganous sulphate the concentration of oxalate ceases to have any effect on the reaction velocity. Hence, the reaction become unimolecular with respect to hexavalent chromium but tends to become zero-molecular with respect to

oxalate, in presence of bivalent manganese as catalyst. The modified path of the reaction has been discussed below :
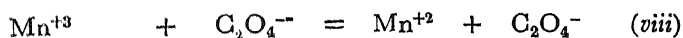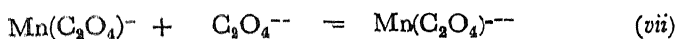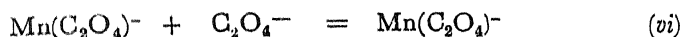
Oxidation of bivalent manganese may be denoted as,

$$CrO_3 + Mn^{+2} = CrO_3^- + Mn^{+3} \qquad (i)$$

$$CrO_3^- + Mn^{+2} = CrO_3^{--} + Mn^{+3} \qquad (ii)$$

Trivalent manganese thus formed is likely to produce complexes with oxalate which may be tepresented by :

$$Mn^{+3} + C_2O_4^{--} \rightleftharpoons Mn(C_2O_4)^+ \qquad (iii)$$

or,

$$Mn^{+3} + 2 C_2O_4^{--} \rightleftharpoons Mn(C_2O_4)^- \qquad (iv)$$
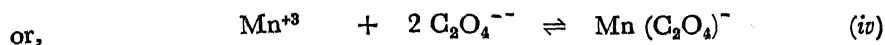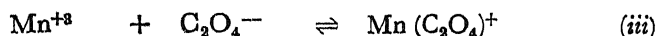
We have already made a study on the oxalate complex formed above,[18] in association with the manganous ion and it is found that the complex is very unstable in a fair acidic solution. But in a low acid concentration the reaction mechanism may correctly be represented by the following scheme :

$$CrO_4^{--} + 2 H^+ = H_2CrO_4$$

$$= H_2O + CrO_3 \qquad (i)$$

$$CrO_3 + C_2O_4^{--} = CrO_3^- + C_2O_4^- \qquad (ii)$$

$$C_2O_4^- + CrO_3 = CrO_3^- + 2 CO_2 \qquad (iii)$$

$$CrO_3^- + Mn^{+2} = Mn^{+3} + CrO_3^{--} \qquad (iv)$$

$$Mn^{+3} + C_2O_4^{--} = Mn(C_2O_4)^+ \qquad (v)$$

$$Mn(C_2O_4)^- + C_2O_4^{--} = Mn(C_2O_4)^- \qquad (vi)$$

$$Mn(C_2O_4)^- + C_2O_4^{--} = Mn(C_2O_4)^{---} \qquad (vii)$$

$$Mn^{+3} + C_2O_4^{--} = Mn^{+2} + C_2O_4^- \qquad (viii)$$

$$Mn^{+3} + C_2O_4^- = Mn^{+2} + 2 CO_2 \qquad (ix)$$
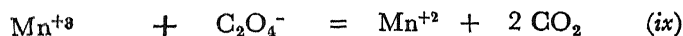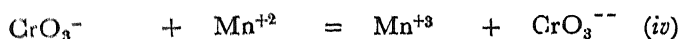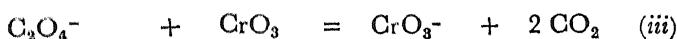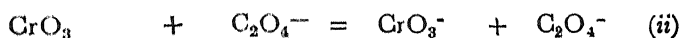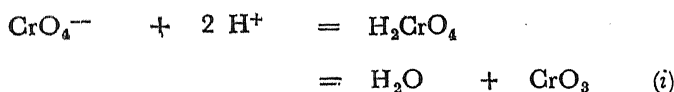
In the above mechanism step no. (iv) is especially true in low acid medium, for in a strong acid solution CrO_3^- will form sufficient quantity of Cr^{+5} which will directly react with oxalate according to the scheme put forward on page 206 of this paper. The oxides of chromium in quadrivalent or trivalent stage is likely to be more basic in character and therefore will more easily form cations. In the presence of oxalate the trivalent manganese quickly from complexes as indicated in steps (v) and (vi). As they are transferred into anion with a negative charge, further oxidation of oxalate which itself is having negative charge, takes place slowly. (step vii). In the oxidation of oxalate therefore, the cation Mn is more active and as has been already said, the reaction will depend on the stability constant of the complex compound.

It is also observed that in low acid medium the red colour due to the formation of trivalent manganese appears in sufficient quantity. It appears that in these circumstances the reaction become of the consecutive type.[11]

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